[2+2] CYCLOADDITIONS OF FLUORINATED METHYLENECYCLOPROPANES AND THE THERMOLYSIS OF 3,4 DIMETHYL 1,1,2,2-TETRAFLUOROCYCLOBUTANE

By

DANIEL DALY

A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN
PARTIAL FULFILLMENT OF THE REQUIREMENTS
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To Sandi and Nellie

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I would like to thank my Research Director Dr. W. R. Dolbier, Jr., for the support and encouragement he has provided during the years of my graduate studies. In my mind he will always retain the title, "The Boss". I would also like to thank B. E. Smart for his help in the synthesis of the methylenecyclopropanes.

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Chairman: William R. Dolbier, Jr.
Major Department: Chemistry

The [2+2] and [4+2] cycloaddition reaction of 2,2 Difluoromethylenecyclopropane 1 and (difluoro)methylene-cyclopropane 2 are reported. Dienes studied are cyclo-pentadiene 3, butadiene 4, furan 5 and diphenylisobenzo-foran 6. 1,1-Dichloro-2,2 difluoroethylene 7 was the only ethylene used.

Reactions of 1 with 3 and 5 gave both exo and endo [4+2] cycloadduct. The reaction of 6 yielded only the endo adduct. The only [2+2] cycloaddition reaction of 1 was with 7.

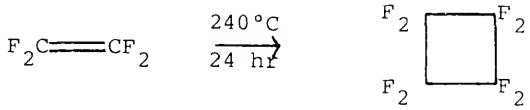
Reaction of 2 and 4 and 7 gave only one [2+2] cyclo-adduct and 2 did not react with any diene in [3+2] fashion.

The thermal decomposition of cis 3,4-dimethyl-1,1,2,2-tetrafluorocyclobutane 8 was investigated. The rate of isomerization to trans-1,2-dimethyl 3,3,4,4-tetrafluorocyclobutane 9 was measured and compared to the rate of dissociation to 3,3-difluoropropene 10. The results are consistent with two-step mechanism involving a diradical intermediate.

SECTION I
INTRODUCTION

Cycloaddition Reactions

In 1946, octafluorocyclobutane 11 was discovered during the polymerization of tetrafluoroethylene 12.[1] When tetrafluoroethylene was placed under the usual polymerization conditions except with a polymerization inhibitor included, the only product recovered was octafluorocyclobutane.[2]

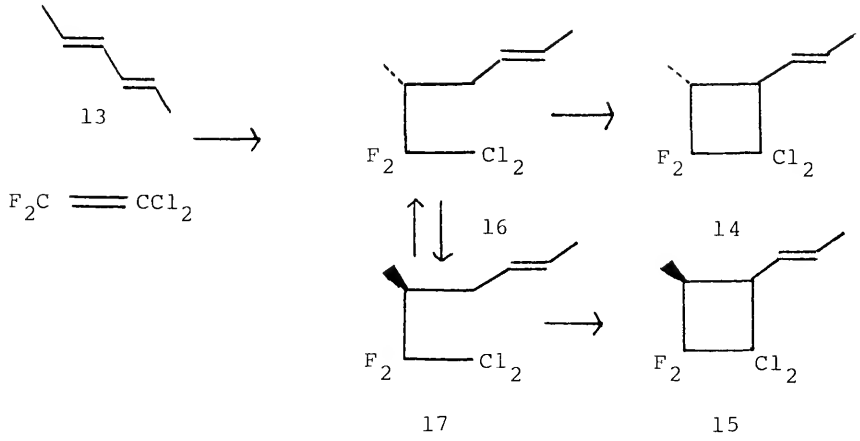


12 11

The mechanism of [2+2] cycloadditions has since been shown to proceed through a two-step process in which there is a diradical intermediate.

In 1964, Bartlett reported a loss of stereochemistry during the [2+2] cycloaddition between 1,1-dichloro-2,2-difluoroethylene and trans,trans-2,4-hexadiene 13.[3] If the reaction were to proceed with retention of configuration,

the only product expected would be 14. However, 14 and 15 were recovered. Thus, after obligatory control studies on olefinic and product stabilities, Bartlett proposed the existence of diradicals 16 and 17.



Every [2+2] cycloaddition reaction covered here will be treated as a two-step process. Although we do not deny that it is possible for such molecules as ketenes and allenes to have a concerted route, we have found all available data for the molecules covered in this paper to support the two-step process as the correct mechanism.

An examination of the potential energy surface of the [2+2] cycloaddition reaction will illustrate the pathway being discussed.

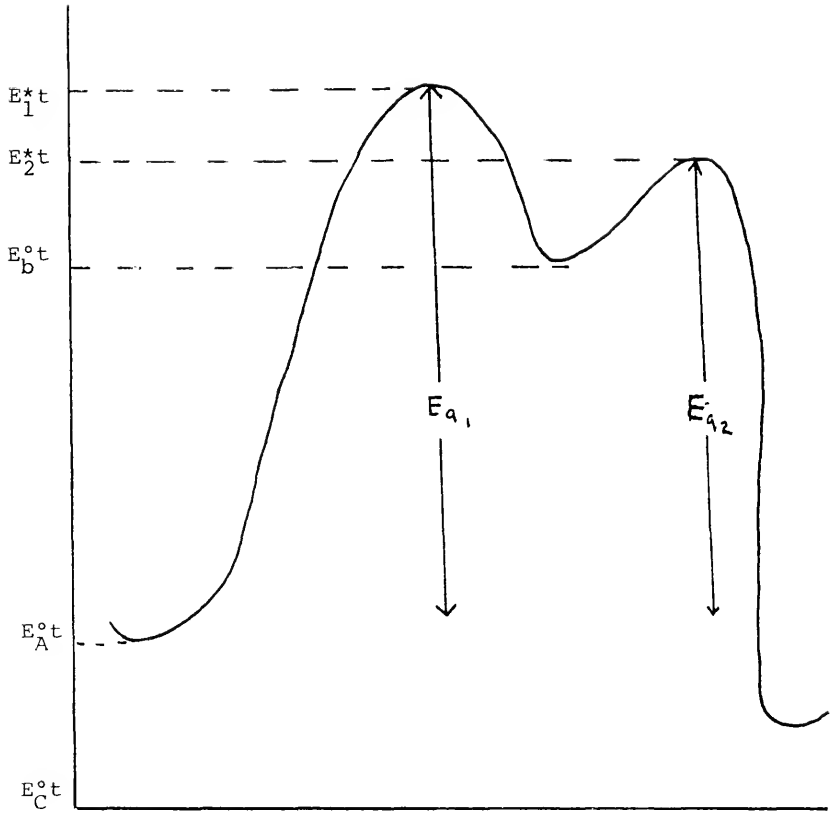


Figure 1. Potential energy surface vs. reaction coordinate. $E_A^{\circ}t$ is the average energy of the olefin at temperature t; $E_B^{\circ}t$ is the average energy of the diradical intermediate at t; $E_C^{\circ}t$ is the average energy of the product at t; $E_t^{\circ *}$ is the energy of the activated complex leading to the diradical intermediate; $E_t^{'*}$ is the energy of the activated complex leading to the product; $E_1^{*}t$ is the energy of activation from olefin to diradical intermediate; $E_2^{*}t$ is the energy of activation from diradical intermediate to product.

Note the transition state leading to the diradical intermediate is of higher energy than the transition state leading to the product($E_t^{\circ *} > E_t^{\prime *}$). This is because the rate-determining step is the first bond formation.[4] Consequently, only those factors affecting the energy levels $E_t^{\circ *}$, $E_A^{\circ}t$, and $E_B^{\circ}t$ will determine whether the olefin will undergo [2+2] cycloaddition reactions.

A somewhat similar approach to analyzing these reactions has been adopted by both Bartlett and Cabrial.[5,6] In 1972, Bartlett listed three properties which olefins must possess in order to undergo [2+2] thermal cycloadditions: (a) exothermicity of double bond opening, (b) stabilization of potential diradicals, and (c) ease of approach of reactants. Bartlett cited the energy difference between the average energy of the olefin, $E_A^{\circ}t$, and the average energy of the product, $E_C^{\circ}t$, as meeting his first criterion of exothermicity of double bond opening. It is contended that a low $E_C^{\circ}t$ is less significant than the energy difference between $E_A^{\circ}t$ and the average energy of the diradical intermediate, $E_B^{\circ}t$. The reason for this contention will become more apparent as the sections on factors influencing $E_A^{\circ}t$ and $E_B^{\circ}t$ are read.

The Average Energy of the Olefin, $E_A^{\circ}t$

Since the discovery of octalfuorocyclobutane, tetrafluoroethylene has been used as a reagent in over

ninety other [2+2] cycloaddition reactions.[7] This fact alone suggests that fluorines have a marked effect on the reactivity of the double bond.

Due to its size relative to carbon and its strong electronegativity, fluorine has an unusual effect on both bond lengths and bond angles as shown in Table I. From Table I it appears that the shortening of the carbon-carbon bond with increasing fluorination is less striking than the effect of geminal fluorine substituents on the FCF bond angle (which is close to tetrahedral). There have been several attempts to explain this effect of fluorines on molecular geometry.

Table I. Bond angles and bond length in fluorinated ethylene.[8]

	CH_2=CHF 18	CH_2=CF_2 19	FHC=CF_2 20	F_2C=CF_2
r(C=C)Å	1.333	1.315	1.309	1.311
r(C-F)Å	1.348	1.323	1.32	1.319
<HCH	120.4	121.8		
<HCF	115.4		116.2	
<FCF		109.3	112.8	112.5

One attempt was by Bent, who proposed that a change in hydridization to more "p" character occurs at the carbon center when a substituent is replaced by a more electronegative one, and that this change is directed towards the more electronegative substituent.[9] Bent's proposal led Bernett to develop a localized molecular orbital theory in which the hybrid atomic orbitals (HAO's) that carbon uses to form bonds with fluorine have more "p" character than those it uses to form bonds with hydrogen or other carbons.[10] Using bond angles, Bernett calculated the corresponding hydrizations shown in Table II. From these figures he concluded that the carbon HAO's used to form the carbon-fluorine bond in gem-difluoro group are sp^3 even when the carbon center is part of a double bond.

Table II. Bond angles and carbon hybridization in fluoromethylene and methylene groups.[9]

	<FCC	<FCH	<HCH	C-Fsp
$CF_2=CH_2$	109°		121.48	3.03
$CF_2=CF_2$	110°			2.92
$CH_2=CHF$	120°54	115.24		2.53
cis-CHF=CHF 21	122	114		2.49

Another attempt to explain fluorine's effect on molecular geometry was by Epiotis, who attributed the change in bond angles to π-non-bonded interaction.[11] He concluded that this interaction favors unequivocally a shrinkage of the FCF bond angle, reasoning that the destabilizing spatial overlap between the fluorine two-p-π atomic arbital (2pHAO) and the 2pHAO of the non-adjacent carbon decreases with decreasing F_1CF_2.

Note that Epiotis's argument stresses fluorine's size relative to carbon, while Bernett's stresses its electronegativity. As a result, Epiotis can account much better for the large difference in carbon-halogen bond strength upon successive halogenation. Table III shows the large differences in bond energies and bond lengths upon successive fluorination versus chorination and bromination. Keep in mind that, according to the Pauling scale of electronegativity, fluorine, chlorine, and bromine have values of four, three, and two-point-eight respectively. Therefore, unless a reason were to be proposed for such small changes in electronegativity's having such a large effect on the type of bond formed, then at least some interaction between non-bonding electrons and carbon centers must be included in any explanation of the exact nature of the carbon-fluorine bond.

To date, no single description of either the exact nature of bonding in fluoroolefins or the effect of fluorines

Table III. Bond dissociation energies for halomethanes[8]

	X=F		X=Cl		X=Br	
	r(C-F) A°	D°(C-F) kcal/mole	r(C-Cl) A°	D°(C-Cl) kcal/mole	r(C-Br) A°	D°(C-Br) kcal/mole
CH_3X	1.385	109.0	1.782	83.7	1.939	69.2
CH_2X_2	1.358	122	1.772	81	1.934	64
CHX_3	1.332	128	1.767	77.7	1.930	62
CX_4	1.317	129.7	1.766	72.9	1.942	56.2

on olefinic behavior has been universally accepted. The two explanations for the pronounced effect of fluorines on olefin reactivity attribute the instability of the fluoro-olefinic system to either (a) the carbon-fluorine bond's being weaker than those on an sp^3 center, or (b) the carbon-carbon double bond's being weaker in the fluoroolefinic system than in others.

On first inspection, the available data seems to support explanation (b). The heats of hydrogenation of 12. 20, and 19 are 16, 8, and 4 kcal/mole greater than ethylene 20.[12] And for tetrafluoroethylene, the heats of addition of chlorine gas, polymerization, and dimerization are 14, 17 and 42 kcal/mole greater than ethylene.[10] However, these results can also be attributed to increasing stabilization of the carbon-fluorine bond by arguing that fluorines are less able to remove "p" electron from an sp^2-hybridized carbon than an sp^3-hybridized one. In fact, Peters used force constants to calculate that the carbon-carbon double bond strength in 12 as about 130 kcal/mole--very close to that of ethylene.[13] So what evidence does exist that fluorine substituents have an effect on $E_A^{\circ}t$?

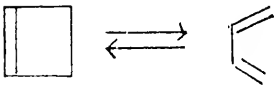
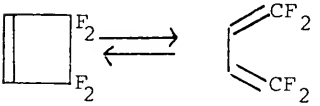
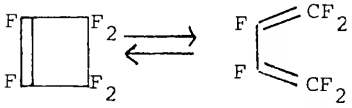
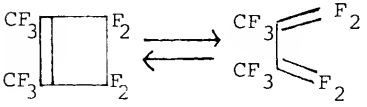
In Table IV, the thermodynamic ΔH values for the thermal cyclobutene ring opening are shown.[8]

The first striking finding is the difference in the thermal rearrangement between cyclobutene 23 and perfluoro-cyclobutene 25. Cyclobutene is quantitatively converted to

butadiene at 200°C. The equilibrium is shifted in the opposite direction in the thermolysis of perfluorobutadiene. Replacing the fluorines in the first and second position with protons again shifts the equilibrium back to the butadiene as can be observed in the thermal rearrangement of 24.[14]

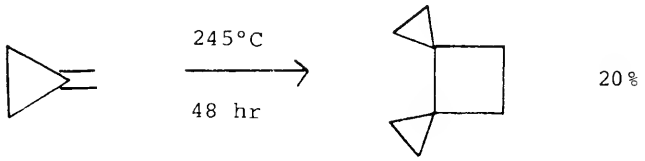
Thus there is a drastic effect on the cyclobutene ⇄ butadiene equilibrium in going from a butadiene with three fluorosubstituents on a double bond to a butadiene with geminal fluorosubstitution on a double bond. This indicates that three fluorines have a definite destabilizing effect on the double bond.

Table IV. Cyclobutene ring opening.[8]

Reaction	Ea kcal/mole	ΔH kcal/mole
	32.7	-8
	47.9	-3
	47.1	11.7
	46.0	.4

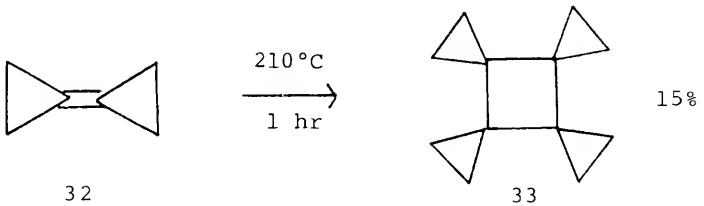
The effect of a gem-difluoro group on $E_A^{\circ}t$ is not obvious. Rodgers calculated the TT-bond dissociation energy for tetrafluoroethylene, 1,1-difluoroethylene, and ethylene to be 52.3 ± 2, 62.1 ± 1.5, and 59.1 + kcal/mole.[15] The 7 kcal/mole difference between 12 and ethylene agrees with other thermodynamic data on tetrafluoroethylene. However, 1,1-difluoroethylene 19 has a 3 kcal/mole greater value than ethylene. This, along with the thermodynamic stability of 25 relative to 24, suggests that the gem-difluoro group has a stabilizing effect on $E_A^{\circ}t$. But the heats of hydrogenation of 19 relative to ethylene suggest destabilization of the olefin.

For a long time after the discovery of 11, it was believed that an olefin had to have at least two fluorine substituents on a double bond in order to undergo a [2+2] cycloaddition. But in 1972, Binger and Dolbier reported the dimerization of methylenecyclopropane 30 in a head-to-head fashion.[16,17]



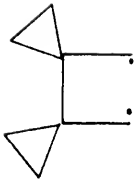
30 31

Methylenecyclopropane has an sp^2 carbon center in a cyclopropyl ring, giving rise to a strain energy of 12 kcal/mole.[18] Destruction of the sp^2 center would relieve this strain and thus provide a strong driving force for the [2+2] cycloaddition reaction. Referring back to Figure 1, the 12 kcal/mole of strain energy would be expressed as a 12 kcal/mole increase in $E_A^{\circ}t$ relative to ethylene. Experimentally, when two cyclopropyl substituents were introduced, as in biscyclopropyledine 32, the reaction proceeded more easily.[19]

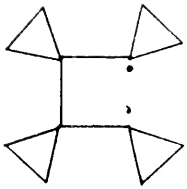


32 33

Taking the simplest of additivity rules for groups, biscyclopropyledine should be destabilized by 24 kcal/mole, 12 kcal per sp^2 center on a cyclopropyl ring relative to ethylene. An increase in reactivity in 32 compared to methylenecyclopropane is interpreted as the additional reactivity introduced by the additional sp^2 center on the ring. The 12 kcal/mole should be more than enough to account for the added destabilization in the diradical intermediate 34 relative to the intermediate 35.



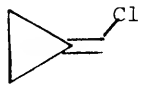
34



35

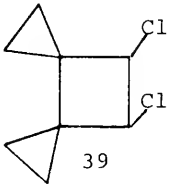
In fact, Benson showed that a radical sites on a cyclopropane ring is approximately 8.5 kcal/mole less stable than a secondary radical.[20]

Similar reaction rates were reported for the dimerizations of chloro-36, bromo-37, and ethoxy-38 methylenecyclopropane.[6]



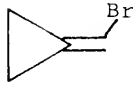
36

188°C
3 hr



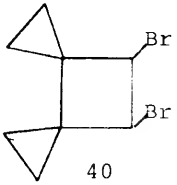
39

59%



37

188°C
3 hr



40

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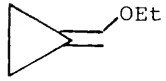

38

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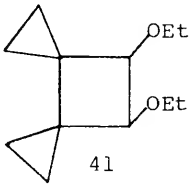
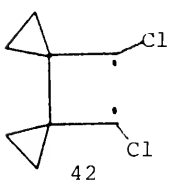
3 hr



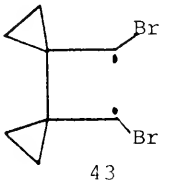
41

88%

This similarity in rates is not surprising since the three olefins have almost identical E_A°t's and the diradical intermediates 42, 43, and 44 are expected to have approximately identical E_B°t's, being stabilized to about the same extent by all three substituents.[21]



42



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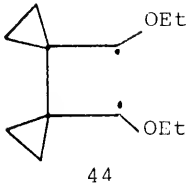


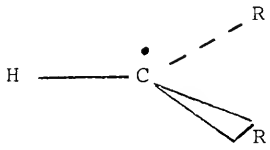
44

However, notice that ethoxymethylenecyclopropane dimerized slightly faster than the other two methylenecyclopropanes. This is due to the fact that ethoxy groups stabilize radicals a little more than chloro or bromo groups do.[22]

In conclusion to this section, it appears that olefins which use the release of strain energy as a driving force for the [2+2] cycloaddition reaction are those with either a methylenecyclopropane group or three or four fluorines. It was shown that an sp^2 center in a cyclopropane ring introduces 12 kcal/mole of strain. However, the quantitative assessment of fluorine substituents has yet to be achieved. This is partly due to the ambiguity concerning the exact role fluorines play in directing olefins via the [2+2] cycloaddition route.

The Average Energy of the Diradical: $E^{\circ}_{B}t$

This discussion will exclude conjugated olefins which yield stable diradicals through resonance, such as allenes, acrylonitrile, and styrene, and instead will cover the following α-substituents, where R is equal to OEt, Br, Cl, H, CH_3, or F.



There is not an overabundance of data on the effect of substituent on carbon radical sites. Experimental methods that have been used to measure the effect of substituents on radical stability have consisted of generating the radical in question by thermal decomposition of either peroxyesters or azocompounds.[23,24] Of course, the measurements obtained apply only to the specific radicals generated, and any comparison of measurements obtained by different methods would not be valid.

However, the heat of formation, ΔH°_{f}, and the stabilization energy, E_s, of free radicals can be estimated by the following methods.[25,26] If the bond dissociation energy, BDE, of a compound XY is defined such that groups X and Y are connected by a bond, then the standard enthalpy change of the below reaction can be considered.

$$XY \rightleftharpoons \dot{X} + \dot{Y}$$

Then, if the enthalpy change, ΔH_1°, of the reaction is measured, the heat of formation of the free radical $\dot{X}$ can be calculated from the heats of formation $H_f^\circ(XY)$ and $H_f^\circ(\dot{Y})$ as shown:

$$\Delta H^\circ = H_f^\circ(X) + H_f^\circ(Y) - H_f^\circ(XY)$$

Additionally, the stabilization energy is given by the equation

$$E_s = H_{BDE}(CH_3 - H) - H_{BDE}(R\text{-}H)$$

which reduces to

$$E_s = H_f^\circ(CH_3^\cdot) - H_f(R^\cdot) - H_f(CH_3 - H) + H_f(R\text{-}H)$$

The error of these calculations is at best ± 1 kcal, and may actually reach ± 5 kcal/mole.

Values of H_{BDE}, H_f°, and $\frac{1}{2} H_{BDE}(H_2)$ were used to construct Table V.

The E_s values calculated from these figures are shown in Table VI.

Table V. Substituents effects on the heat formation ($\Delta H_f^\cdot$) of the methyl radical.[26]

Molecule		$\Delta H_f^\cdot$(R-H)	$\Delta H_f^\cdot$(H·)	$\Delta H_{BDE}^\cdot$	$\Delta H_f^\cdot$(R·)
CH_3- H	45	-17.9	52.3	102	34.4
CH_2Cl-H	46	-20.63	52.3	98.1	25.2
CH_1Cl_2-H	47	-22.8	52.3	100.8	15.7
CCl_3-H	48	-24.2	52.3	90	13.5
CF_3-H	49	-166.71	52.3	102	-112.5
CH_3CF_2-H	50	-117.7	52.3		
CH_2Br-H	51	-9.00	52.3	99	37.7
CH_2O -G	52	-51.73	52.3	92.3	-11.75

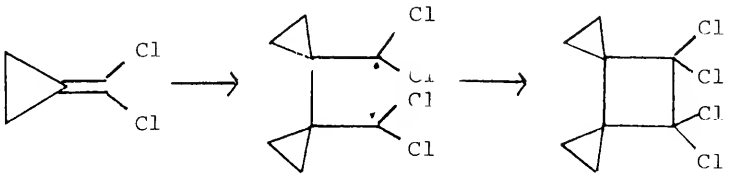
Unfortunately, there are no available data on the bond dissociation of CHF_2-H 53 or CH_2F-H 54. But there are data on the $H_f(R^{\cdot})$ of $CH_3CF_2^{\cdot}$ 55 permitting the calcualtion of $H_{BDE}(CH_3CF_2\text{-}H)$ shown in the table,[27] and both Dolbier and Benson have concluded that the effect of gem-difluoro substituents is very small.[28,29]

The demonstration of the effect of gem-dichloro groups on the rate of [2+2] cycloaddition was accomplished by Dolbier in 1968. Dichloromethylenecyclopropane 56 dimerized at 100°C for 8 hours is greater than 95% yield. Compared to the conditions of 240°C for 48 hours required for just 20% yield of parent methylenecyclopropane, and the condition of 140°-150°C and 12 hours for 34, 35 + 36 the added stabilization in the diradical intermediate of 58 appears to be very dramatic.

Table VI. Energies of stabilization (E_S) for substituted methyl radicals.[27]

radical	E_S (kcal/mole)
$CH_3\cdot$	0
$CH_2Cl\cdot$	6.46
$CHCl_2\cdot$	13.97
$CCl_3\cdot$	14.59
$CF_3\cdot$	-1.92
$CH_3CF_2\cdot$	-1.69
$\cdot CH_2OCH_3$	11
$CH_2Br\cdot$	5.59

From Table VI, the E_s values of $CH_2Cl^{\cdot}$, $\dot{C}H_2OCH_3$, and $CH_2Br^{\cdot}$ are nearly the same, $\dot{C}H_2OCH_3$ being slightly more stable. This is consistent with Cabral's results, where he found 1-ethoxymethylenecyclopropane to be a little more reactive than 1-chloromethylenecyclopropane and 1-bromomethylenecyclopropane, but less reactive than dichloromethylenecyclopropane.

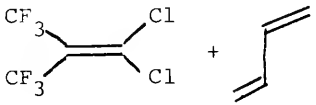


The E_s values calculated for the radicals seem to agree at least qualitatively with the [2+2] cycloaddition results, since an increase in E_s is correlated with an increase in rate of the cycloaddition reaction. This rate increase can be explained with a reference back to Figure 1, where the deeper the "well" of the diradical intermediate, the more likely the occurrence of the cycloaddition reaction.

But what are the forces causing a barrier between the energy level of the olefin, $E^{\circ}_{A}t$, and that of the biradical intermediate, $E^{\circ}_{B}t$?

It is conceivable that there are olefins which meet the energetic requirements for [2+2] cylcoaddition but do not have a low energy "path" along the reaction

coordinate between the valleys near the average energies of the olefin $E_A^{\circ}t$ and $E_B^{\circ}t$. This is what Bartlett called steric hindrance to approach of reactants. In 1972, Bartlett attempted to cycloadd butadiene to 1,1-Bis(trifluoromethyl)-2,2-dichloroethylene 59, but was unable to get any cycloadduct.[30] He concluded that the failure to undergo a [2+2] cycloaddition reaction was due to steric inhibition of the transition state leading to the diradical intermediate. In the same year, Dolbier reported that dimethylmethylenecyclopropane 60, 60 did not dimerize upon heating to a temperature of 245°C for 80 hours.[17]



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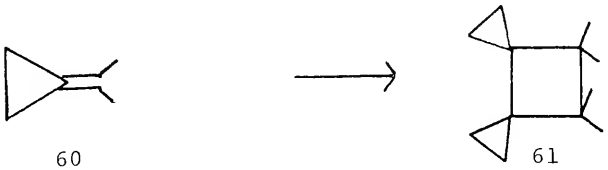
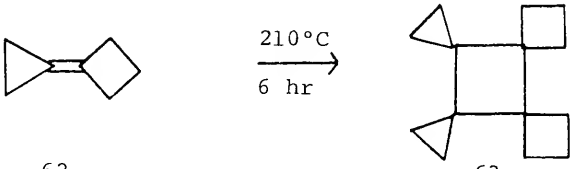


60 61

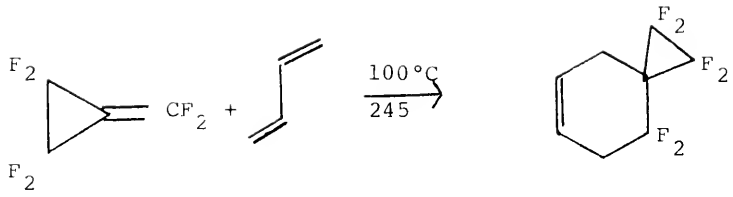
Interestingly, Dolbier proposed that the dimethyl substituents cause enough Van der Waals repulsion through non-bonding interaction to impede the formation of the diradical intermediate. But if this non-bonding interaction was reduced by "tied back" methyl, as in cyclopropylidinecyclobutane 62, the reaction occurred.



62 63

But does 62 dimerize because of the decrease in Van der Waal's repulsive forces or the increase in olefin strain energy in going from 60 to 62? If the former is true, then 62 dimerization may represent the limiting case for steric inhibition of [2+2] cycloaddition reactions.

In 1976, Smart was unable to dimerize perfluoromethylenecyclopropane 61.[31] He was also unable to get butadiene to add to 64 in a [2+2] fashion. In fact, the only cycloadduct he was able to isolate was 65, which is the expected product from the [4+2] cycloaddition. Smart concluded that steric inhibition to approach was caused by fluorines on the ring.



64 65

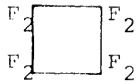
In an attempt to gain further insight into the effects of exothermicity of double bond opening, stabilization of potential diradicals, and ease of approach of reactants, the [2+2] cycloaddition reactions of difluoromethylenecyclopropane and 2,2-difluoromethylenecyclopropane were investigated. The results of these reactions will be discussed in SECTION II.

Cyclobutane Thermolysis

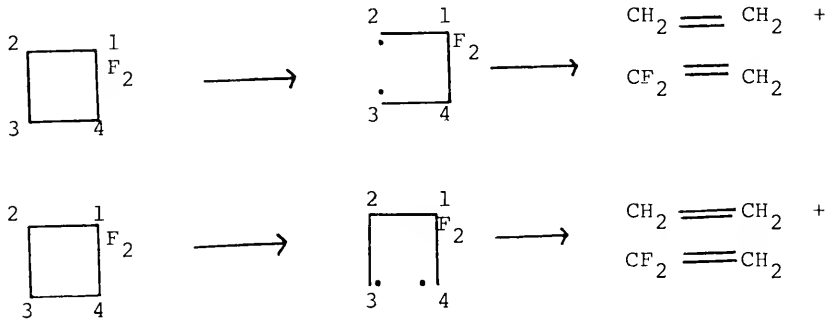
Cyclobutanes and alkylcyclobutanes are model compounds for unimolecular thermal decomposition and have been studied extensively for this reason.[32,33] Substituent effects on cyclobutane ring thermolysis have considerable mechanistic interest, since the parent system has been thoroughly elaborated. In fact, the rate of decomposition is a direct measurement of the effect of a particular substituent on

carbon-carbon single bond strength. For example, previous studies have shown that perfluorocyclobutane decomposes at a slower rate than cyclobutane 66 itself.[34] Note that the activation energies of these decompositions differ by 15.5 kcal. Since the systems have a similar preexponential "A" factor, the fluorine substituents must raise the bond energies of the cyclobutane molecule. Frey studied the thermal decomposition of 1,1-difluorocyclobutane 67 and 1,1,2,2-tetrafluorocyclobutane 68 and came to the same conclusion. His results along with those previously mentioned, are presented in Table VII.[35,36] The rates relative to perfluorocyclobutane were calculated from the above Arrhenius parameters at 500°C. Frey proposed a two-step mechanism to explain his results. The first step is bond breakage of the weaker carbon-carbon single bond (a bond without fluoro substituents) forming a diradical intermediate, followed by cleavage of a second stronger bond (a bond with fluoro substituents). Based on this mechanism the following conclusions can be made from the results shown in Table VII. The decomposition of 1,1,-difluorocyclobutane has a statistical factor of twice that of the symmetrical decomposition of 1,1,2,2-tetrafluorocyclobutane and a relative rate of 2.5. This would suggest similar energetics, since the rate-determining step for dissociation would be cleavage of the second stronger bond. Then the two cyclobutanes have similar C_1 - C_2 carbon-carbon bond strengths. This is consistent

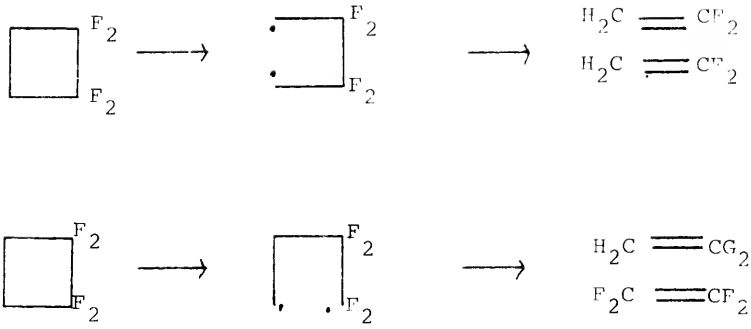
Table VII. Cyclobutanes Thermal Decompositions [35]

Molecule	Log A	Ea kcal/mole	Relative rate
 → $2CH_2 = CH_2$	15.6	62.5	862
66			
 F_2 → $CF_2 = CH_2$ + $CH_2 = CH_2$	15.61	69.24	10.8
67			
 F_2 → $2CF_2 = CH_2$	15.35	69.79	4.2
F_2			
68			
 F_2 → $CF_2 = CF_2$ +	15.27	73.64	.29
F_2 $CH_2 = CH_2$			
69			
 F_2 → $2CF_2 = CF_2$	15.97	74.24	1.00
F_2 F_2			
11			

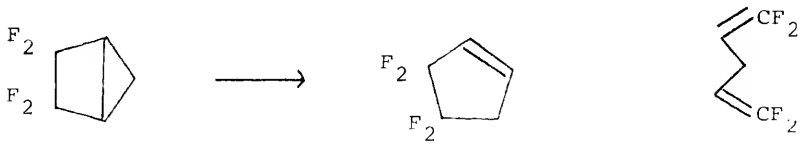
with the energetics of the unsymmetrical fragmentation of 68 and the fragmentation of 11, which are also similar. The reduction in rate of the symmetrical fragmentation of 68 compared to 66 would be attributed to the increase in carbon-carbon bond strength due to the α-substituents which would result in a retardation of the second bond cleavage. Thus the low activation energy pathway



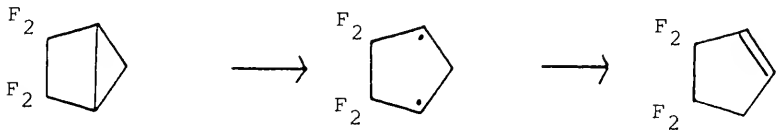
(symmetrical cleavage) of 68 involves the cleavage of first a carbon-carbon bond that is only slightly stronger than those in cyclobutane. This cleavage yileds a diradical intermediate such as 71, and is folowed by the breakage of a stronber carbon-carbon bond, yielding two molecules of difluoroethylene. The high activation energy decomposition pathway of the cyclobutane involves first the cleavage of a strong carbon-carbon bond. This yields the intermediate 72, and unsymmetrical products are then formed by cleavage of a second strong carbon-carbon bond.



To examine the proposed low energy pathyway, and thus the mecahnism of cyclobutane decomposition, Dolbier and Al-Fekri investigated the effect of gem-difluoro substituents on C_3-C_4 carbon-carbon bond strength.[37] The system they used was 3,3,4,4-tetrafluorobicyclo[2.1.0] pentane 73, which thermally isomerizes in the gas phase to 3,3,4,4-tetrafluorocyclopentene 74 and a small amount of 1,1,5,5-tetrafluoro-1,4-pentadiene 75.

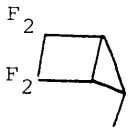


A comparison with the analogous rearrangement in the hydrocarbon system indicated a definite rate retardation (Ea = 7.6 kcal/mole).[38] The mechanism of the rearrangement of 73 is presumed to proceed via the intermediacy of 76. To determine whether the step being retarded by the fluoro-substituent was the initial bond breaking to



76

form the diradical or a proton shift from the diradical to the cyclopentene, the thermal interconversion of endo- and exo-5-methyl-2,2,3,3-tetrafluorobicyclo[2.1.0] pentanes, 77 and 78 were studied. A comparison of the data from this study with the data from a study of similar hydrocarbons (Chesick and Baldwin) clearly indicated that the 1,2 hydrogen shift was responsible for the differing activation energies.[39,40] Thus, the effect of gem-difluoro-substituents on carbon-carbon bond strength was shown to be insignificant.



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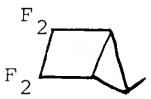

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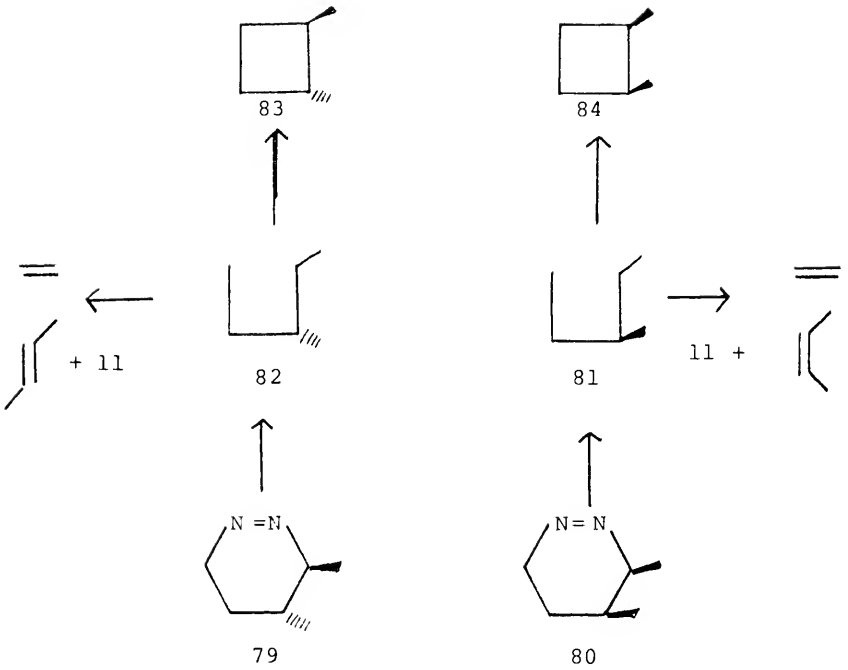
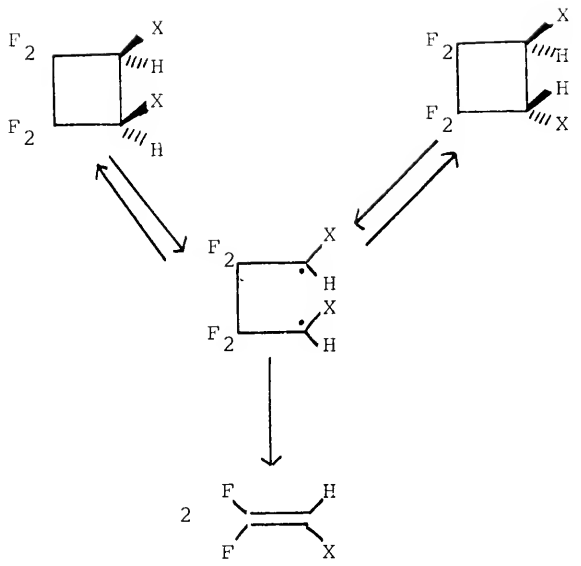
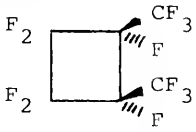


This would give credance to Frey's two-step process where the bonds to the fluoro-substituent would cleave first. Evidence for the existence of a diradical intermediate was provided by Dervan.[41] He thermally decomposed the cis- and trans-3,4-dimethyl-3,4,5,6-tetrahydropyridazine 79 and 80, at 415°C, and determined the relative rates of cleavage, closure, and rotation of the 1,4-diradicals generated. These rate constants gave the same distribution of the two butenes found in the thermolysis of cis- and trans-1,2-dimethylcyclobutane 83 and 84; thus, the same diradical appears to be generated from two different sources.[42]



Further evidence for the existence of a diradical intermediate is provided by the observation of isomerization of 1,2-disubstituted cyclobutanes. The probability of observing the rotation of a diradical is directly related to the hindrance of dissociation. The ideal system to observe this isomerization would then be the 1,2-disubstitued-3,3,4,4-terafluorocyclobutanes. By placing gem-di-fluoro-substituents in the 3 and 4 position and thus strengthening the C_3-C_4 carbon-carbon bond, dissociation would be retarded, while cleavage of the C_1-C_2 carbon-carbon bond would not be affected by the fluoro-substituents.

Table VIII. Kinetic parameters of 1,2-disubstituted cyclobutane thermal decomposition.



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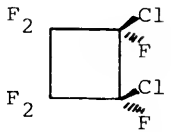

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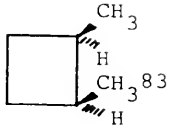


83

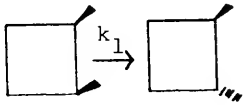
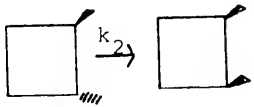
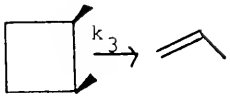
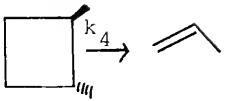
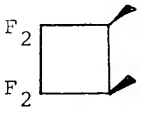
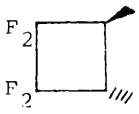
	Ea(kcal/mole	LogA	Ea(kcal/mole)	LogA	Eq(kcal/mole)	LogA
	64.2	15.36	60.2	15.09	60.1	14.00
	64.2	15.67	60.2	14.85	61.3	14.56
	64.2	15.07	65.3	15.49	60.4	15.48
	64.2	15.63	65.3	15.07	61.6	15.47

Table VIII shows the kinetic parameters of three 1,2-di-substituted cyclobutanes. Note that for cis-1,2-bistrifluoromethylhexafluorocyclobutane 85 and cis-1,2-dichlorohexafluorocyclobutane 86, the rate constants of isomerization to trans-1,2 bistrifluoromethylhexafluorocyclobutane 87 and trans 1,2 dichlorohexafluorocyclobutane 88 are lower than the rate constants for dissociation, while for 1,2-dimethylcyclobutane, the reverse is true.[43]

Thus, strengthening the C_3-C_4 carbon-carbon single bond did decrease the rate of dissociation compared to isomerization. However, in both 85 and 86 there was a single fluoro substituent on carbons 1 and 2, which would strengthen the C_1-C_2 carbon-carbon bond. In an attempt to further elucidate the role of fluoro substituents on the rate of dissociation and isomerization, the thermolysis



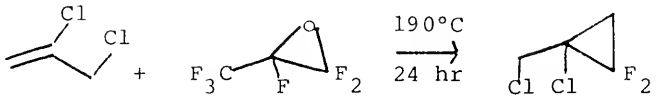


of cis- and trans-3,4-dimethyl-1,1,2,2-tetrafluorocyclobutane was measured. It was thought that this system would optimize the conditions in which the rate of isomerization would be greater than the rate of dissociation and hopefully generate a model system for investigation of carbon-carbon bond strength and diradical stability.

SECTION II
RESULTS

Synthesis of 2,2-Difluoromethylenecyclopropane and 1,1-Difluoromethylenecyclopropane

Dried 2,3-dichloropropene 89 was placed in an autoclave along with an excess of hexafluoropropylene oxide 90. This reaction mixture was heated for twenty-four hours at 190°C. The product, 1-(chloromethyl)-1-chloro-2,2-difluorocyclopropane, 91, was isolated by distillation and characterized by ^{1}H NMR, ^{19}F NMR, and IR. Product 91 was slowly added to a round-bottom flask containing excess zinc, a



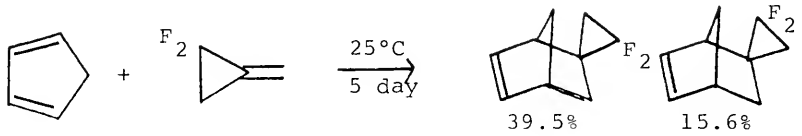
89 90 91

catalytic amount of zinc chloride and DMSO. This mixture was heated to a temperature of 150°C at which point an exothermic reaction took place and 2,2-difluoromethylenecyclo-

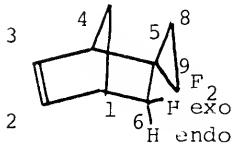
propane began condensing in a dry ice trap. 2,2-Difluoromethylenecyclopropane was placed in an evacuated glass reaction vessel and heated to 350°C. After twenty-five minutes the reaction mixture was collected and characterized as 1,1-difluoromethylenecyclopropane by ^{1}H NMR and ^{19}F NMR.

Cycloaddition Reaction of 2,2-Difluoromethylenecyclopropane

The cycloaddition reactions were carried out in a sealed, glass tube containing 1 and an excess of olefin. In this manner, 1 was allowed to react with an excess of cyclopentadiene 92 for five days at room temperature, yielding a 2:1 molar mixture of endo- and exo-isomers of the [4+2] cycloadduct. The two isomeric products were separated by glpc and characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, IR, and mass spec. In the proton NMR there is a characteristic



difference in the chemical shifts of the C_6 endo and exo protons ($\Delta\delta H_{6x}-H_{6n}$) in the two isomers 93 and 94, which allows identification. The parent norbornene, 95, has unique



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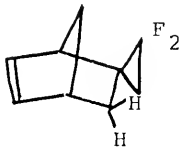
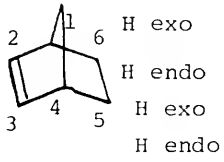


94

spectral properties including a shielding factor for the endo protons on carbons 5 and 6.[44]



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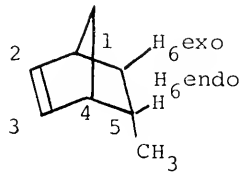
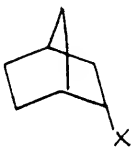
The chemical shifts for the endo- and the exo- C_5 and C_6 protons are .96 and 1.57 ppm downfield from TMS. This difference depends upon substitution in the C_5 position. In compound 96, the effect of the substitution in the fifth position can be seen in the dramatic difference it



96

produces in the chemical shift.[44] The C_6 endo- and exo- protons of norbornene are separated by .74 ppm ($\Delta\delta H_x-H_n$). A similar difference is seen in the compound 96, where $\Delta\delta H_x-H_n$ = .86 ppm.

To determine the source(s) of shielding, Foster and McIvor studied the effects of C_5 substitutents on the chemical shifts of the C_6 endo- proton of bicyclo[2.2.1]hept-2-enes and bicyclo[2.2.1]heptanes.[44] Table IX shows the differences in the chemical shifts of the C_6 endo-protons that they reported.



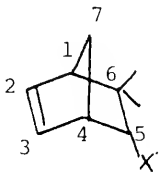


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Table IX. Chemical shifts of C_6 endoprotons of bicyclo[2.2.1]hept-2-ene and bicyclo[2.2.1]heptane.[44]

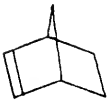
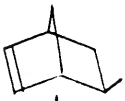
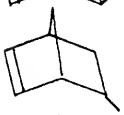
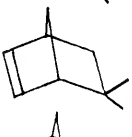
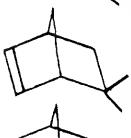
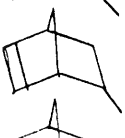
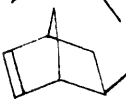
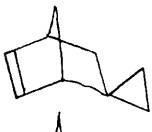
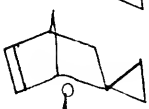
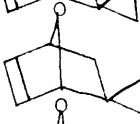
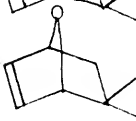
I	II	III	IV
X	1	2	1-2
OH	9.50	9.37	.13 ppm
H	9.54	9.36	.18 ppm
OAc	9.43	9.31	.12 ppm
Br	9.40	9.30	.10 ppm

From these results, Foster and McIvor concluded that the C_6 endo-proton was subjected to two shielding sources, one being the diamagnetic anisotropy of the double bond, and the other being the C_5-C_8 bond.

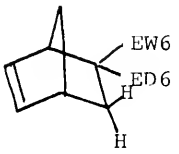
The upfield shift due to the double bond is shown in Column IV of Table IX, the average of which is .13 ppm. Foster and McIvor estimated the shielding effect of the C_5-C_8 bond as seen in the comparison of the endo-proton chemical shifts of the compounds 95 and 96 to be .5 ppm. Unfortunately, they did not study the effects of the exo-substituent on the exo-proton.

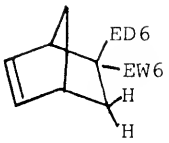
A comparison of values in Column II, Table IX demonstrates the effect of an electron-withdrawing substituent on the shielding effectiveness of the C_5-C_8 single bond. It appears that as the electron density of the C_5-C_8 bond shifts towards the C_3 nucleus, the ability of this bond to shield the C_6 protons decreases. A comparison of the effects of different substituents on the chemical shifts

Table X. The chemical shifts of the C_6-exo and C_6-endo protons on C_5-substituted norbornenes.[45,46]

		C_6-endo proton (ppm)	C_6-exo proton (ppm)	$\Delta\delta_{H_{6X}-H_{6N}}$ (ppm)
	95	.96	1.61	.65
	96	1.2	.98	.22
	97	.46	1.84	1.38
	100	1.04	2.24	1.2
	101	1.70	1.40	.3
	98	1.13	1.95	.82
	99	1.38	1.69	.31
	93	1.60	1.50	.1
	94	1.10	2.10	1.0
	102	1.60	1.96	.36
	103	1.25	2.26	1.01

of the two C_6 protons is made in Table X. The reasons for these particular substituents being compared will become clearer after careful examination of the molecules being characterized.





EW = Electron withdrawing

ED = Electron donating

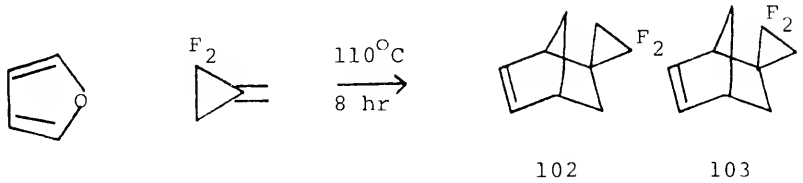
The identification of these isomers is made simple by the following rationale. Since the shielding ability of the C_5-C_8 and C_5-C_9 single bonds depends on the electron-withdrawing substituents at the C_8 and C_9 positions, the C_5-C_9 bond should produce more shielding. Therefore, the major isomer 93 is expected to experience more shielding at the C_6 exo- than the C_6 endo- position. Of course, the C_6 endo-proton experiences the shielding influence of the double bond. Thus, with an approximation of the difference in shielding produced by the C_5-C_8 and C_5-C_9 bonds, an estimation of the $\Delta\delta$ expected between the two C_6 protons can be made. We can approximate the shielding effect of the C_5-C_9 bond to be .8, based on the difference in endo shifts of 96 + 97 (which are .46 and 1.2).

There has been no demonstration of the effect of gem-difluoro substituents on the shielding influence of the C_5-C_8 bond of these bicyclo[2.2.1]hept-2-enes. However, Gaede and Balthazor reported the chemical shifts of endo- and exo-5-(trifluoromethyl)bicyclo[2.2.1]hept-2-ene, 98 and 99, shown in Table X.[45]

Comparing the difference in shielding of the C_6 protons of 96 and 97 with the difference between 98 and 99, it appears that a decrease in shielding has been caused by the 3 fluorines, this difference being about .5 ppm, or .16 ppm per fluorine. Thus, the major isomer 93 of the cyclopentadiene reaction should have a small $\Delta\delta$ due to both the decrease in shielding of the C_6 endo proton by the C_5-C_8 bond and to the "normal" shielding of the C_6 exo proton by the C_5-C_9 single bond. If one assumes that the cyclopropane single bond can be treated as a normal carbon-carbon bond (which it cannot) and that the effect of fluorines on the shielding ability of the C_5-C_8 bond is additive, then the difference in chemical shifts of the two isomers can be calculated. The C_6 exo- C_6 endo- value for norbornene, .61 ppm, was used to approximate the shielding effect of the olefin. So for compound 93's C_6 exo proton, an upfield shift of .8 ppm occurs due to the C_5-C_9 cyclopropyl bond. And for its C_6 endo proton, a total upfield shift of 1.09 ppm occurs, representing .61 ppm plus .48 ppm from the C_5-C_8 cyclopropyl bond. The theoretical $\Delta\delta H_{6x}$-H_{6n} is therefore .28. The observed value was .1 ppm.

For the minor isomer 94, the C_6 exo proton should experience a 0.48 ppm upfield shift from the C - C cyclopropyl bond and the C_6 endo proton should have a net upfield shift of 1.41 ppm, 0.61 ppm from the double bond and 0.8 ppm from the C -C bond. The expected $\Delta\delta H_{6x}-H_{6n}$ value is thus 0.93 ppm. The observed value was 1.0 ppm.

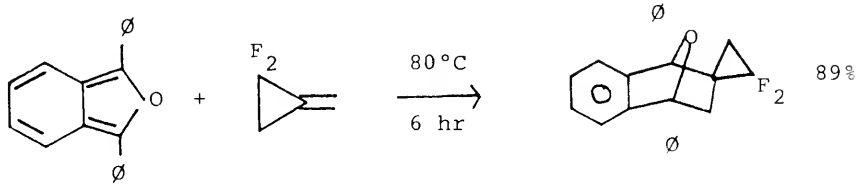
2,2-Difluoromethylenecylcopropane was reacted with excess furan 104 in a sealed tube at 110°C for 8 hours. The mixture (21.2%, isolated yield) contained two isomers in a ratio of 6:1. The isomers were separated and characterized by ^1H NMR, ^{19}F NMR, ^{13}C NMR, IR, and mass spec. Again it is obvious that the two isomers are [4+2] cycloadducts. The assignment of endo and exo isomers was again based on the chemical shift difference between the endo and exo proton in the C_6 position. The endo isomer 102 has an observed $\Delta\delta H_{6x}-H_{6n}$ of 0.36 ppm. The theoretical value, ignoring the effect of oxygen, is 0.28 ppm. For the exo isomer 103 the observed value was 1.1 ppm and the theoretical value was 0.96 ppm.



102 103

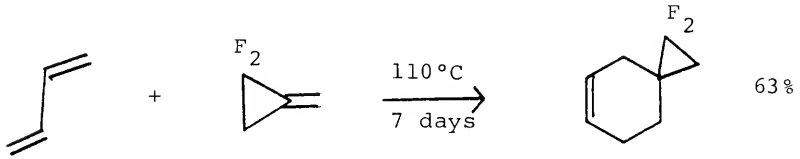
The reaction of diphenylisobenzofuran 105 and 1 was performed in chloroform at 80°C for 6 hours. Interestingly, only one product was isolated and in 89% yield. This product was identified by; ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, IR and mass spec. A [4+2] cycloadduct was again the only product isolated, but surprisingly only one isomer was discovered. The product was identified by its small $\Delta\delta H_{6x}-H_{6n}$ value, which was 0.4 ppm.

The possibility of an unstable exo isomer being formed was checked by stopping the reaction after 2 hours, upon which a ^{19}F NMR of the product mixture indicated the presence of two AB patterns in a 9:1 ratio. Other evidence that the exo adduct of diphenylisobenzofuran may be thermally unstable derives from the observation of the thermal instability of the exo adduct from the furan reaction. When the exo adduct of furan, 103, was heated, neat at 120°C for 3 hours, it decomposed almost entirely into two molecules. Each molecule had approximately the same retention times as furan and 1, but was not either of these substances.



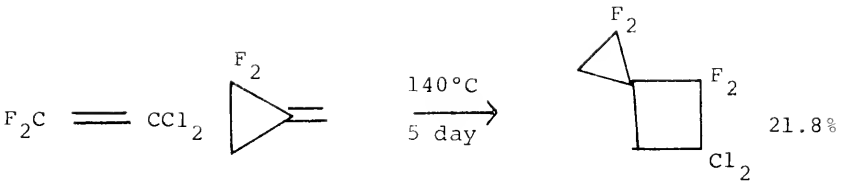
105 106

Butadiene and 1 were reacted for seven days at 110°C in a sealed tube. The [4+2] cycloadduct was collected and characterized by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, IR and mass spec. The characteristic spectral features are the olefinic protons in the ^{1}H NMR, which appeared at 6.0 ppm as a broad singlet. Also, integration reveals four allylic protons.



107

The only [2+2] cycloadduct obtained for 1 was from its cycloaddition reaction with 1.1-dichloro-2,2-difluoroethylene. Excess olefin along with 1 was reacted in a sealed tube at 140°C for 5 days. The only product isolated other than the dimer of dichlorodifluoroethylene was the [2+2] cycloadduct 108. This product was isolated and identified by ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, IR and mass spec. The characteristic spectral features of the ^{19}F NMR were

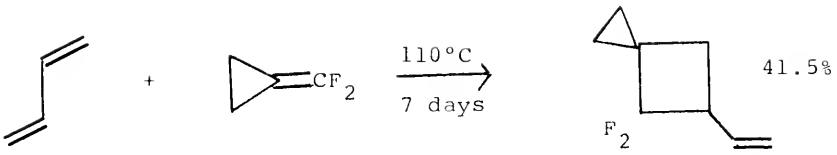


108

two AB patterns, each with characteristic chemical shifts of +100.87 and +139.4 ppm upfield of $CFCl_3$. These correspond to cyclobutyl and cyclopropyl fluorines respectively. In addition, the ^1H NMR showed two cyclobutyl and two cyclopropyl protons.

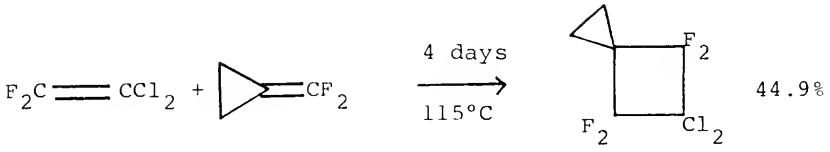
Cycloaddition Reactions of(Difluoro)methylenecyclopropane

(Difluoro)methylenecyclopropane was allowed to react with excess butadiene in a sealed tube at 115° for three days. The only product isolated, other than the butadiene dimer, was 109. It was obvious from the vinylic region in the proton



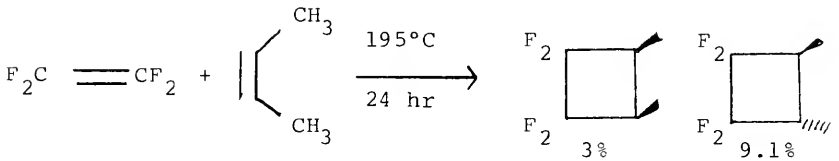
spectrum, that the product was a [2+2] cycloadduct. In the ^{19}F NMR an AB pattern was observed with a chemical shift of 102.37, which is characteristic of gem-difluoro substituents on a cyclopropyl ring.

In the reaction of 2 with 1,1-dichloro-2,2-difluoroethylene only one product was isolated, besides the dimer of dichlorodifluoroethylene. The product was identified by ^{1}H NMR, ^{19}F NMR, Ir and mass spec. The spectral characteristics of this symmetrical product were the singlet peaks in both the ^{1}H NMR and ^{19}F NMR.



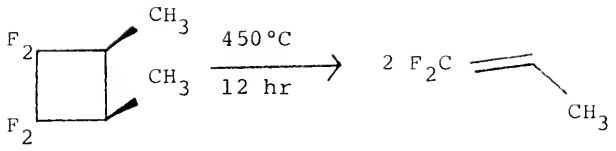
Kinetics of Cyclobutane Thermolysis

A two-fold excess of cis-2-butene was condensed into a 500 ml autoclave along with tetrafluoroethylene. This mixture was allowed to react at 200°C for 24 hours. The product mixture (10% isolated yield) was composed of two isomers in a ratio of 2:3, where the trans-cyclobutane was the major isomer. The isomers 8 and 9 were isolated and characterized by their ^{1}H NMR, ^{19}F NMR, ^{13}C NMR, IR and mass spec.



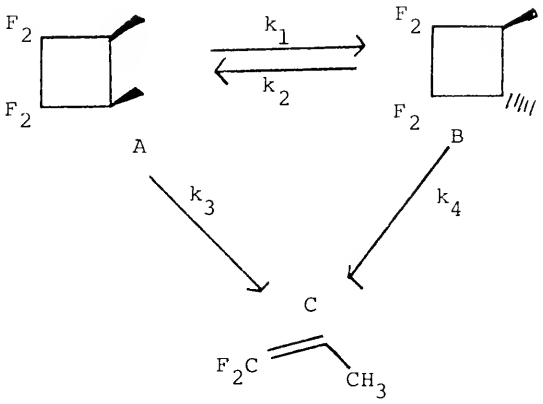
8 9

The submerged reaction vessel was charged with 8 and allowed to react for 12 hours at 450°C. The reaction mixture was then collected and characterized by ^{1}H NMR, ^{19}F NMR and mass spec. The mass spec, proton and fluorine NMR were consistent with that already reported for difluoropropene.[47]



Each kinetic run was performed on pure cis-3,4-dimethyl-1,1,2,2-tetrafluorocyclobutane. The reactions were carried out in the gas phase in a vessel which is connected to a vacuum line and submerged in a molten salt bath. The temperature of the salt bath was varied between 434.75°C and 483°C during the nine kinetic runs. Gas samples were taken at equal time intervals depending upon the rate of the reaction, such that each sampling had similar concentrations for each run. Thus, if a run at 435°C had samples removed at 30 minute intervals, a run at 470°C would have samples removed at 10 minute intervals. This was done to get similar concentration values for all three molecules for each run. This was found to keep the error in GC analysis at a constant value making comparison between runs more precise. Each sample was injected four times and the average concentration was the actual data point used. The determination of the rate constants for the

following kinetic scheme was assumed and rate constants obtained using a method of optimization called Simplex. The program which used this method of optimization



calculated the concentration of A, B and C and compared them to the experimental values. The formulas used in both programs "Approx" and "Improve" to calculate the concentration of A, B and C are given below.

$$A/A^\circ = 1 - \frac{1}{\lambda_1 - \lambda_2} \quad \frac{\lambda_2 T_1}{\theta_1}(e^{-\theta_1 t} - 1) - \frac{\lambda_1 T_2}{\theta_2}(e^{-\theta_2 t} - 1)$$

$$B/A^\circ = \frac{1}{\lambda_1 - \lambda_2} \frac{T_1}{\theta_1}(e^{-\theta_1 t} - 1) - T_{2/\theta_2}(e^{-\theta_2 t} - 1)$$

$$C/A^{\circ} = \frac{1}{\lambda_1 - \lambda_2} \left[(\lambda_2 - 1)\frac{T_1}{\theta_1}(e^{-\theta_1 t} - 1) - (\lambda_1 - 1)\frac{T_2}{\theta_2}(e^{-\theta_2 t} - 1) \right]$$

where $S_1 = k_1 + k_3 \qquad S_2 = k_2 + k_4$

$$\theta_1 = \frac{S_1 + S_2}{2} + \left[\frac{(S_1 - S_2)^2}{4} + k_1 k_2 \right]^{\frac{1}{2}}, \quad \theta_2 = \frac{S_1 S_2}{2} - \left[\frac{(S_1 - S_2)^2}{4} + k_1 k_2 \right]^{\frac{1}{2}}$$

$$\lambda_1 = \frac{k_2}{S_2 - \theta_1} \quad , \quad \lambda_2 = \frac{k_2}{S_2 - \theta_2}$$

$$T_1 = S_1 - k_1 \lambda_1 \quad , \quad T_2 = S_1 - k_1 \lambda_2$$

Table XI. Rate constants obtained from Simplex program for the respective temperatures.

Temperature (°C)	$k_1(sec^{-1})$	$k_2(sec^{-1})$	$k_3(sec^{-1})$	$k_4(sec^{-1})$
434.75	$9.19x10^{-5}$	$3.5x10^{-5}$	$1.09x10^{-5}$	$4.19x10^{-5}$
441	$1.53x10^{-4}$	$5.75x10^{-5}$	$1.98x10^{-5}$	$6.67x10^{-6}$
444.7	$1.63x10^{-4}$	$5.92x10^{-5}$	$2.13x10^{-5}$	$8.24x10^{-6}$
450.2	$2.305x10^{-4}$	$8.056x10^{-5}$	$2.89x10^{-5}$	$1.16x10^{-5}$
461.3	$4.26x10^{-4}$	$1.68x10^{-4}$	$5.67x10^{-5}$	$1.83x10^{-5}$
467.25	$6.15x10^{-4}$	$2.46x10^{-4}$	$9.4x10^{-5}$	$2.55x10^{-5}$
472.2	$7.74x10^{-4}$	$2.97x10^{-4}$	$1.07x10^{-4}$	$3.7x10^{-5}$
479	$1.17x10^{-3}$	$4.60x10^{-4}$	$1.62x10^{-4}$	$6.5x10^{-5}$
483	$1.48x10^{-3}$	$6.10x10^{-4}$	$1.90x10^{-4}$	$1.01x10^{-4}$

Table XII. Arrhenius parameters for 3,4 dimethyl-1,1,2,2-tetrafluorocyclobutane.

Rate Constants	Ea kcal/mole	Log A
k_1	59.8	14.43
k_2	60.8	14.3
k_3	62.9	14.47
k_4	65.2	14.73

SECTION III
DISCUSSION

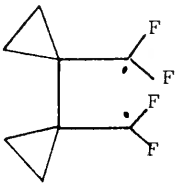
Cycloaddition Reactions

The failure of difluoromethylenecyclopropane to dimerize was somewhat surprising considering the three factors which seem to govern [2+2] cycloaddition reactions. The energy level $E_A^{\circ}T$ should be at least 12 kcal/mole higher than ethylene's due to the introduction of an sp^2 center in a cyclopropyl ring. And the effect of two fluorines on the double bond should not appreciably affect its stability. Therefore, difluoromethylenecyclopropane should be as reactive as the parent methylenecyclopropane, which does dimerize.

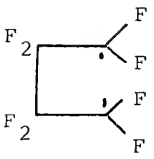
Interestingly, difluoromethylenecyclopropane does undergo [2+2] cycloaddition with butadiene, 1,1-dichloro-2, 2-difluoroethylene, and bromotrifuloroethylene, while methylenecyclopropane does not react with butadiene. This suggests that steric hindrance to approach is a reasonable explanation for failure of dimerization. In fact, difluoromethylenecyclopropane and dimethylmethylenecyclopropane may represent

olefins that approach or even reach the steric limit for inhibition. The fact that 2 reacts in a [2+2] fashion with other molecules places it very close to the limiting condition. This could yield some information about the activated complex leading to the diradical intermediate. The steric inhibition to cyclobutane must occur in the rate-determining step which is the initial bond formation. The other possibility is that first bond formation occurs, but the steric repulsion preventing the second bond formation is too great to overcome, causing the diradical intermediate to revert back to the reactants. This implies that there is at least a 3 kcal difference in the activation energy for closure versus return, which is inconsistent with data obtained from observation of the behavior of similar diradicals.

During the dimerization of difluoromethylenecyclopropane, the potential diradical would have the structure 111 below:



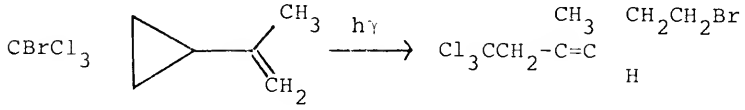
111



112

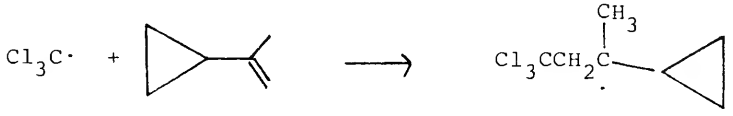
Compare the structure of 111 to that of 112. The closure of either of the diradicals should require about the same activation energy. So it is hard to explain why the closure of diradical 111 requires at least 3 kcal more than the return to the olefin while the closure of diradical 112 seems to occur at a significant rate-as indicated by the observation of cyclobutane product in fairly high yield. Dolbier mentioned that the lifetime of the diradical intermediate must be short, since no rearrangement of the cyclopropylcarbinyl radical occurs.[17] The opening of the cyclopropylcarbinyl radical is thought to be a low energy process and has been observed in other studies.

Huyser and Taliaferro reported the opening of this radical during the photochemically induced reaction between bromotrichloromethane 113 and 2-cyclopropylpropene 114.[48]

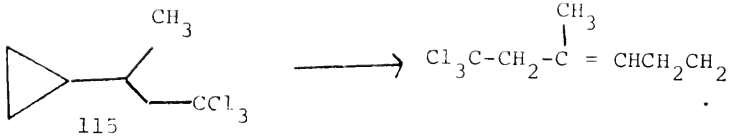


113 114

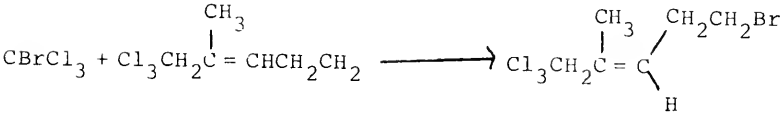
The mechansim of this reaction is shown below.



115



115



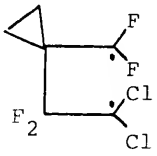
116

CCl_3·

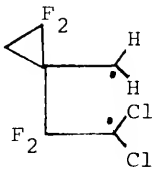
Kochi, Krusic, and Eaton reported the generation of the cyclopropylcarbinyl radical by hydrogen abstraction with t-butoxy radical during the photolysis of di-t-butylperoxide 117 with cyclopropane as solvent.[49] This hydrogen abstraction, and subsequent homoallylic rearrangement, was followed by ESR. The opening to the allyl carbinyl radical took place at low temperature. Therefore, the opening of the cyclopropylcarbinyl radical seems to represent the fate of any "long living" diradical intermediate.

We can only conclude that if the diradical intermediate is formed, then a cyclobutane product is observed. This implies that the first bond formation is the process retarded by steric interactions either between intermolecular fluorines during the dimerization reaction of difluoromethylenecyclopropane or between intermolecular methyls during the dimerization of dimethylmethylenecyclopropane.

A comparison of the reaction conditions of 1,1-difluoro-2,2-dichloroethylene with 1 and 2 reveals some interesting facts about these two molecules. In our results, it was shown that 2 reacted much faster than 1. Thus, having two fluorines on the double bond accelerated the reaction. From the E_s values calculated for $CH_3\dot{C}F_2$ and $CH_3\dot{C}H_2$, diradicals 118 and 119 should not differ greatly in stability.



118

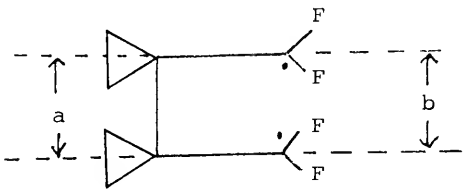


119

The E_s value for $CH_3CF_2\cdot$ was only 1.69 kcal less than that of $CH_3CH_2\cdot$. The steric hindrance to approach would differ between 1 and 2, but based on the steric interactions previously discussed, 119 should close more quickly than 118. Furthermore, when reactions between 1 and 2 with bromotrifluoroethylene were attempted, only difluoromethylene cyclopropane reacted. Therefore we propose that, at least in this case, the gem-difluoro groups have a destabilizing effect on the olefin. Note that this conclusion is based on the original premise that product stability plays an insignificant role in determining reaction rate.

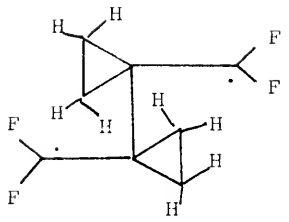
Proof that these groups are involved lies in the observation that the parent compound does dimerize, but the above compounds do not. This rules out the possibility that the steric repulsion is between the protons of the cyclopropyl rings.

From these arguments, information about the structure of the activated complex leading to the below structure can be obtained.



a ≠ b

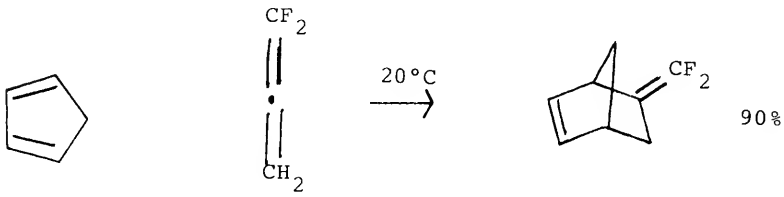
The spatial arrangement of the olefins must be very similar to that expected in a non synchronous concerted pathway, where the distance between the potential bonding sites closely approximates the bond lengths in the cyclobutane product. This rationale also accounts for the steric retardation of [2+2] cycloaddition reactions and the absence of rearranged cyclopropylcarbinyl radicals. Note another possibility for the structure of the diradical intermediate is the transoid conformer shown below.



Rotation of this intermediate could be inhibited by the cyclopropyl protons and thus the inability of difluoromethylenecyclopropane to dimerize would be due to this inhibition of rotation. However, if this is the preferred conformation of the diradical intermediate it is hard to rationalize the extremely different conditions for dimerization of the dichloromethylenecyclopropane and methylenecyclopropane. One would be forced to either state that this difference is due to radical stability, thus proposing a long-lived diradical or different conformation of the two different radicals.

Unfortunately, no other [2+2] cycloaddition reactions were carried out with dimethylmethylenecyclopropane, for it would certainly be interesting to see whether 60 would react with butadiene in a [2+2] fashion.

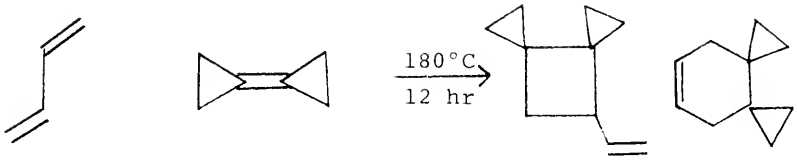
In the reaction of 2 with butadiene, no [4+2] cycloadduct was observed. Gem-difluoro substituents have been shown to have an inhibiting effect on the dienophilicity of the olefin. When Burkholder reacted 1,1-difluoroallene 120 with cyclopentadiene, he isolated only one product, despite the thermodynamic stability gained by fluorine as it went from an sp^2 to an sp^3 carbon



center.[50] However, when Smart reacted butadiene with hexafluoromethylenecyclopropane, it reacted in a [4+2] fashion only. Was this enhanced olefin reactivity due to the four fluorines on the cyclopropyl ring?

When 2,2-difluoromethylenecyclopropane reacted with butadiene, the only cycloadduct isolated was from a [4+2] cycloaddition reaction, and the reaction conditions were fairly mild. Thus, the gem-difluorocyclopropyl substituents must enhance reactivity of methylenecyclopropane towards the [4+2] cycloaddition.

Kaufman and de Meijere in 1973 demonstrated that methylenecyclopropanes favor the [2+2] versus the [4+2] route by reacting biscyclopropylidiene with butadiene.[51]



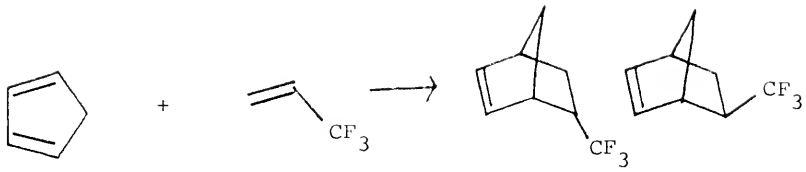
122 123

92 : 8

But the fact that Smart was unable to get perfluoromethylenecyclopropane to undergo and [2+2] but was able to get [4+2] cycloaddition suggests that the fluorines on the ring are capable of sterically inhibiting a [2+2] and activating a [4+2] cycloaddition reaction.

The steric hindrance of the two cyclopropyl fluorines is seen in the [4+2] cycloaddition reactions of 1 with cyclopentadiene and furan. In both cases, the minor isomer obtained has the fluorines in the exo position, where they could be expected to interact with either the 2 protons on the cyclopentadiene ring or the oxygen on the furan ring.

Gaede and Balthazor reported the influence of a trifluoromethyl substituent on the stereochemistry of the Diels-Alder reactions between cyclopentadiene and 3,3,3-trifluoropropene 124.[45]



124 98 99

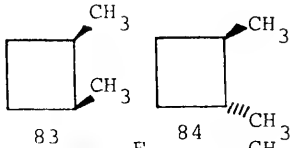
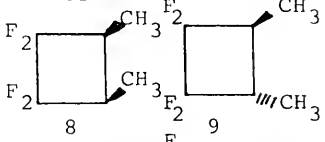
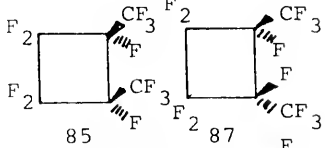
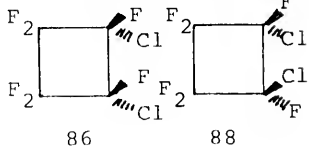
3 : 1

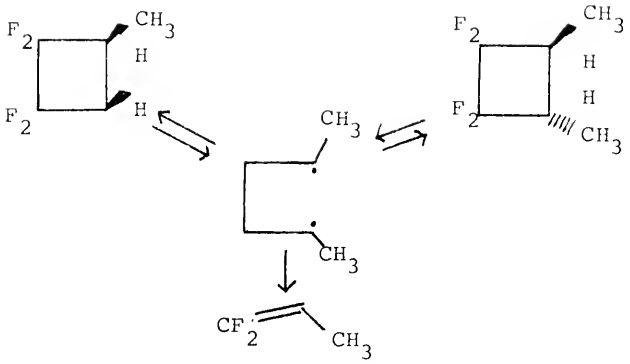
A reasonable explanation of the endo-directing influence of the trifluoromethyl group is the steric interaction between it and the methylene protons of cyclopentadiene in the exo-transition state. So fluorines do influence steric approach.

Cyclobutane Thermolysis

The results of the thermolysis of cis-1,2-dimethyl-3,3,4,4-tetrafluorocyclobutane 8 are consistent with those of thermolysis of other 1,2 disubstituted cyclobutanes, and can best be explained by the 2-step mechanism. According to Frey's mechanism, the weakest bond breaks first, followed by the cleavage of a second, stronger bond. The weakest bond in 8 is the C_1-C_2 bond, as evidenced by the facts that only symmetrical cleavage to the difluoropropene is observed and that 8's rate of isomerization was faster than the rate of dissociation. Therefore, the data for the thermolysis of 3 supports the following mechanism, mechanistic scheme.

Table XIII. Comparison of kinetic parameters of 1,2-disubstituted cyclobutane thermal decomposition.[43]

cis	trans	$Ea_{isomerization}$ (kcal/mole) cis	$Ea_{isomerization}$ (kcal/mole) trans	$Ea_{dissociation}$ (kcal/mole) cis	$Ea_{dissociation}$ (kcal/mole) trans
 83	84	60.1	61.3	60.4	61.6
 8	9	59.8	60.8	62.9	65.2
 85	87	64.2	64.2	64.2	64.2
 86	88	60.2	60.2	65.3	65.3



The activation parameters of 8 in comparison to other 1,2 disubstituted cyclobutanes are shown in Table XIII.

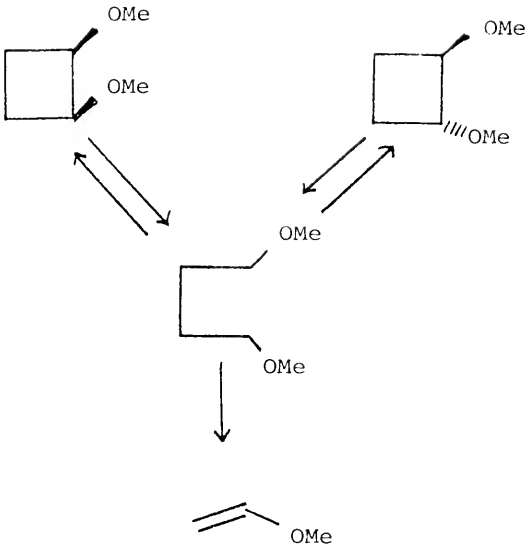
The Ea for isomerization is interpreted as the activation energy required to break the first bond, and the Ea for dissociation as the energy needed to break the second bond. Thus, Table XI shows the effect of substituent on carbon-carbon bond strength and/or diradical stability. Comparing the Ea for isomerization of 8 and that of 9, and of 83 with that of 84, it appears that β-fluoro substituents indeed have no effect on carbon-carbon stability, as shown previously by Dolbier. However, the effect of α-substituents is significant, as shown by the increase in Ea for dissociation of all the cyclobutanes with tetrafluoro-substituents over the Ea's for dissociation of the cis- and trans-dimethylcyclobutanes. Thus, it is clear that gem-difluoro substituents

increase the strength of the carbon-carbon bond toward thermolysis, causing isomerization to occur at a faster rate than dissociation.

The effect of radical stability on isomerization is seen by comparing the Ea for isomerization of 85 with that of 86, and of 87 with 88. Note that replacing a CF_3 group with a Cl group causes a decrease in Ea of approximately 4 kcal/mole.

For the thermolysis of cis-1,2-dimethoxycyclobutane 126 Kirmse and Murawski reported the Ea for isomerization of the cis-isomer to be 55.3 kcal/mole.[52] This is about 5 kcal lower than for the same rearrangement in dimethylcyclobutane. But, unfortunately, the authors did not measure the rate of isomerization of trans->cis, leaving two possible explanations for the decrease in Ea. One explanation is the increase in radical stability resulting from a methoxy instead of a methyl substituent. The other is a larger steric repulsive force between the two cis-methoxy than between the cis-methyl substituents.

The greater repulsion between the two cis-methoxy groups is evidenced by the reported relative rates of dissociation from cis->olefin and trans->olefin. These rates were 10:1 at 351.3°C for 126 and 127, but only 2.65:1 at 430°C for 8 and 9. Therefore, the 1,2-disubstituted 3,3,4,4-tetrafluorocyclobutane may represent a model system for the comparison of diradical stabilities, especially



when the relative stabilities of the cis and trans 1,2-disubstituted cyclobutanes are known.

The greater amount of steric repulsion between cis than trans dimethyl substitutents is seen by comparing the Ea for isomerization of cis to trans with trans to cis for 8 and 9, and for 83 with 84. This steric repulsion accounts for the fact that the cis- dimethyl isomer of both cyclobutane and 1,1,2,2-tetrafluorocyclobutane

underwent dissociation faster than the trans- isomer. Note that replacing the methyl with trifluoromethyl substituents, as in hexafluoro-1,2-bistrifluoromethyl-cyclobutane, alleviates this strain and the difference in Ea vanishes.

The reaction coordinate energy diagram for the thermolyses of 8 and 9 is shown below.

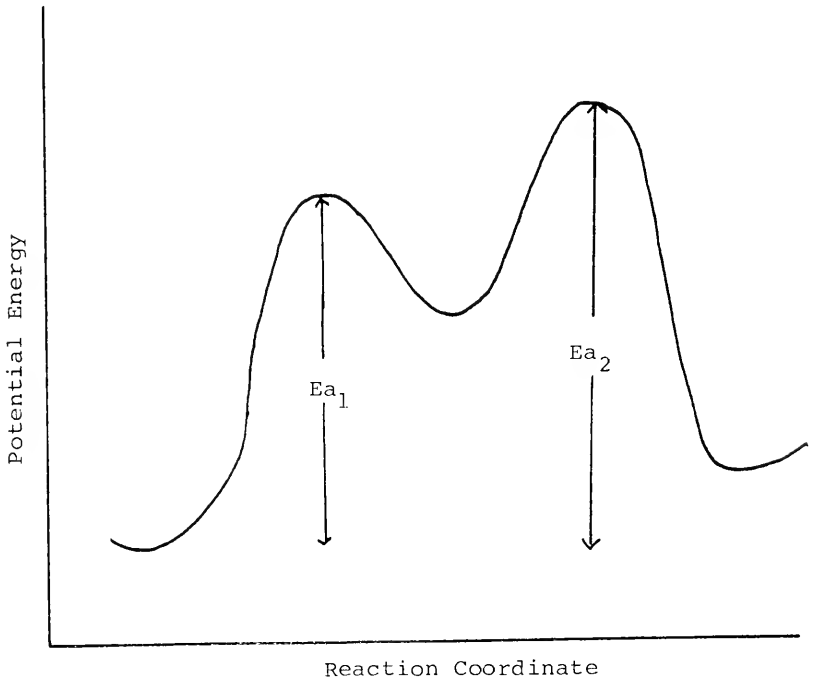


Figure 2. Potential energy surface vs. reaction coordinate.

Ea, is the activation energy for the first bond breakage of the cis isomer; Ea_2 is the energy for the first bond breakage of the trans isomer; and $Ea_3 + Ea_4$ is the energy of activation for the second bond breakage leading to the olefin. The assumption that the diradical intermediates of both isomers have the same average energies is based on intuition, for, once the C_1-C_2 bond is broken and rotation allowed to occur, if is hard to envision any differences in steric repulsion between the two isomers.

Of course, one does not necessarily have to conclude that carbon-carbon bond strength increases with fluoro-substituents. A reasonable rationale for the increase in Ea for the thermolysis of cyclobutane upon fluorination is that the activated complex leading to the olefin is higher in energy when fluoro substituents are on the carbon centers that undergo a hybridization change from sp^3 to sp^2. Thus, one could conclude that the increase in Ea is due to the carbon-fluorine, not the carbon-carbon bond. However this point reduces to a matter of semantics.

SECTION IV
EXPERIMENTAL

Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer and absorption bands are reported in cm^{-1}. The spectra were determined as a film between KBr plates.

The 60 MHz ^{1}H NMR spectra were determined on a Varian EM 360L spectrometer; 100MHz spectra were determined on a Varian XL-100 instrument. Chemical shifts are reported in ppm downfield of internal TMS in $CDCl_3$ solution.

The ^{19}F NMR spectra were determined on a Varian XL-100 instrument. Chemical shifts are reported in ppm upfield of internal $CFCl_3$ in $CDCl_3$ solution.

The ^{13}C NMR spectra were determined on the Varian XL-100 instrument. Chemical shifts are reported in ppm downfield of internal TMS in $CDCl_3$ solution.

Mass spectra were determined on an AEI-MS 30 spectrometer at 70eV. Exact masses were also determined on the AEI-MS 30.

The GLPC analyses and preparative separations were performed on a Varian Aerograph 90-P gas chromatograph with thermal conductivity detector. The gas phase

samples were analysed using a Hewlett-Packard 5710A gas chromatograph with flame ionization detector in conjunction with a Hewlett-Packard 3380S recording integrator.

Procedures

1-(Chloromethyl)-chloro-2,2-difluorocyclopropane 91

A five hundred mL stainless steel rocker bomb was charged with 35.0 g(0.272 mole) of dried 2,3-dichloropropene and 60.0g(0.362 mole) of hexafluoropropylene oxide and heated at 189°C for 24 hours. The bomb was then placed in a cold water bath and cooled to room temperature. After careful ventilation the bomb was opened and washed with 62mL of CH_2Cl_2. The resulting solution was then washed with first water, then a saturated NaCl solution and dried over $MgSO_4$. The CH_2Cl_2 and other lower boiling compounds were removed by rotary evaporation. The residual solution was then fractionated, yielding 31.2g(73.5%) of 91, bp 62-64°C: ^1H NMR (60 MHz, $CDCl_3$)δ1.83(cyclopropyl CH_2, mutiplet), 3.83(CH_2, doublet of multiplet, 2H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=135.6 ppm (midpoint), AB with further splitting, J_{ab}=159 Hz, $\Delta\nu_{ab}$=1473.28 Hz.

2,2-Difluoromethylenecyclopropane 1

A five hundred mL round-bottom flask was equipped with a mechanical stirrer, a pressure-equalized addition funnel, and distillation column, which was attached to two traps, one at 0°C and the other at -78°C. The flask was charged with three hundred mL of dried dimethylsulfoxide, 86.0g(1.1 mole) of zinc dust and 16.5g(0.164 mole) of anhydrous zinc chloride. This mixture was stirred until an oil bath temperature of 155°C was reached and maintained for an hour. Then 41.4g(0.205 mole) of 91 was slowly added, with foaming and bubbling occurring on addition as evidence of the exothermicity of this reaction. The pot temperature should not exceed 160°C. The reaction mixture was heated for three hours at 155°C. At higher temperature dimethylsulfide is given off at such a large rate that the ice bath will not collect all the dimethylsulfide and it will begin condensing in the dry ice trap, contaminating the product. After three hours the addition funnel was quickly removed and a N_2 gas inlet was installed. The system was then allowed to react under N_2 for an additional two hours. Thus, 11.2g of distillate was collected in the dry ice trap. This mixture was carefully refractionated to give 10.0g(54.2%) of 2,2-difluoromethylenecyclopropane: ^1H NMR and ^{19}F NMR are identical to that reported by Fielder[53]; ^1H NMR(100 MHz, $CDCl_3$) δ1.84-2.06 (CH_2, multiplet, 2H), 5.58-5.78(CH, multiplet, 1H), 5.92-6.12

(CH, multiplet, 1H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=137.2 ppm (midpoint), AB with further splitting, J_{ab}=152.0 Hz, $\Delta\nu_{ab}$=1432.1 Hz.

One hundred torr of 1 was placed in a reaction vessel, which was submerged in a molten salt bath at 305°C. This reaction was carried out for 20 minutes. The reaction mixture was then collected in a glass tube which was at liquid N_2 temperature. This glass tube was then sealed under vacuum and placed in a dry ice bath, where it was quickly opened and stoppered with a septum. Separation was achieved by glpc. Seventy percent of this reaction mixture was collected and identified as 2. The column used was a 20% SE-30 column(70 mL/min, He), Tc=25°C: ^1H NMR(100 MHz, $CDCl_3$) δ1.26-1.51(CH_2, triplet, 4H); ^{19}F NMR(60 MHz, $CDCl_3$)ϕ=105.3 ppm (midpoint), AB pattern J_{ab}=57.8 Hz, $\Delta\nu_{ab}$=490 Hz.

Endo- and Exo-1,1-difluorospiro[bicyclo[2.2.1]]-hept-2-ene-6.2'-cyclopropane 93 and 94

One hundred mL of 3a,4,7,7a-tetrahydro-4,7 methanoindene (dicyclopentadiene) was placed in a two hundred mL round-bottom flask equipped with a magnetic stirring bar and distillation column. The flask was then placed in an oil bath and heated to 210°C with vigorous stirring. At this temperature, cracking occurred and product was observed to distill between 60-62°C. The cyclopentadiene was collected in a receiving glask at -78°C.

Into an evacuated glass tube at liquid N_2 temperature, 0.141g(2.14×10^{-3}mole) of cyclopentadiene was condensed along with 0.096g(1.07×10^{-3}mole) of 1. The tube was sealed under vacuum and allowed to warm to room temperature. After five days at room temperature, the tube was placed in a dry ice bath, opened and quickly stoppered with a septum, allowing injections to be made into a glpc with a syringe at -78°C. Separation of the reaction mixture was accomplished using a ¼"x15' 20% TCP column(60mL/min, He), Tc=115°C. The retention time for the endo and exo isomers of the [4+2] cycloadduct were 19 and 22 minutes respectively. Thus 0.066lg(39.5%) of the second product peak was collected and identified as 93: ^{1}H NMR(100 MHz, $CDCl_3$)δ6.14-6.22(vinylic, CH, complex multiplet, 2H) 3.02(CH, singlet, 1H), 2.5(CH, singlet, 1H), 1.51-1.76(CH_2, complex multiplet, 4H), 1.0-1.2(complex multiple, 2H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=136.51 ppm (midpoint), AB with further splitting, J_{ab}=155.775 Hz, $\Delta\nu_{ab}$=1101.68 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ42.2 (C_1,s), 136.9(C_2,s), 134.6(C_3,s), 48.1(C_4,s), 34.5(C_5,s), 34.0(C_6,t,$^2J_{cf}$=9.12 Hz), 49.3(C_7,s), 20.58(C_8,t,$^2J_{cf}$=10.24 Hz), 115.8(C_9,t,J_{cf}=287.82 Hz); IR(neat), 700, 890, 1005, 1150, 1470 cm^{-1}; Mass spectrum gave M^+=156.0738±.0008(5.6 ppm), calculated for $C_9H_{10}F_2$ 156.0750 dev .0012(7.9 ppm).

Also 0.026g(15.6%) of the smaller component was collected and identified as 94: ^{1}H NMR(100 MHz, $CDCl_3$)δ6.12(CH, doublet of doublets, 2H), 3.0(CH, singlet, 1H), 2.6(CH, singlet, 1H),

2.1(CH, complex multiplet, 1H), 1.3-1.5(CH_2, complex multiplet, 3H), 0.9-1.2(CH_2, complex multiplet, 2H): ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=135.73 ppm (midpoint), AB with further splitting, J_{ab}=153.73 Hz, $\Delta\nu_{ab}$=1123.73 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ42.7(C_1,s), 136.9 (C_2,s), 134.6(C_3,s), 48.1(C_4,s), 34.5(C_5,s), 34.0(C_6,t,$^2J_{CF}$= 9.12 Hz), 49.3(C_7,s), 18.56(C_8,t,$^2J_{cf}$=10.3 Hz), 115.8 (C_9,t,J_{cf}=287.8 Hz); IR(neat) 700, 890, 1005, 1150, 1470 cm^{-1}; Mass spectrum gave M^+=156.074$\pm$.0018(12 ppm), calculated for $C_9H_{10}F_2$ dev .0005(3.3 ppm).

Endo-1,1-difluorospiro[oxabicyclo[2.2.1]]hexa-2-ene-6 2' cyclopropane 102 and Exo-1,1-difluorospiro[oxabicyclo[2.2.1] hexa-5-ene 103

The same sealed tube procedure as described above was used to react 0.392g($5.76x10^{-3}$mole) of furan and 0.1296g ($1.44x10^{-3}$mole) of 1 for 4 hours at 140°C. Separation was performed using a ¼"x20' 20% TCP column(72mL/min, He), Tc=125°C. The retention time for the endo and exo isomers of the [4+2] cycloadducts were 20 and 22 minutes respectively. Thus 0.079g(18.2%) of the first peak was collected and identified as 102: ^1H NMR(100 MHz, $CDCl_3$)δ6.55-6.45(CH, multiplet, 2H), 5.12(CH, doublet, 1H), 4.55(CH, singlet, 1H), 1.9-2.1(CH_{exo}, complex multiplet, 1H), 1.38-1.71(CH_2, complex multiplet, 3H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=134.35 ppm (midpoint), AB with further splitting, J_{ab}=152.8 Hz, $\Delta\nu_{ab}$=1981.11 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ79.8(C_1,s), 136.3 (C_2,s), 134.3(C_3,s), 82.2(C_4,s), 33.3(C_5,s), 33.7(C_6,t,$^2J_{CF}$=

9.8 Hz), 20.09(C_7,t,$^2J_{CF}$=10.2 Hz), 113(C_8,t,J_{CF}=280.2 Hz); IR(neat), 885, 910, 1110, 1120, 1380 cm^{-1}; Mass spectrum gave M^+ 157.0465±.0026(17 ppm), calculated for $C_8H_7F_2O$ 156.0465 dev 0.00001(-.02 ppm).

Also, 0.007g(3%) of the second component was collected and identified as 103: ^1H NMR(100 MHz, $CDCl_3$)δ6.56(CH, doublet of doublets, 1H), 6.45(CH, doublet of doublets, 1H), 5.13(CH, doublet, 1H), 4.70(CH, singlet, 1H), 2.3(CH_2, complex multiplet, 1H), 1.12-1.34(CH_2, complex multiplet, 3H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=135.21 ppm (midpoint), AB with further splitting, J_{ab}=154.75 Hz, $\Delta\nu_{ab}$=1998.7 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ80.2(C_1,s), 139.2(C_2,s), 135.4(C_3,s), 80.8(C_4,s), 34.2(C_5,s), 34.4(C_6,t,$^2J_{CF}$=10.1 Hz), 17.52(C_7,t,$^2J_{CF}$=10.32 Hz), 113.5(C_8,t,J_{CF}=287.1 Hz); IR (neat) 660, 890, 910, 1090, 1210, 1370 cm^{-1}; Mass spectrum gave M^+ 157.0470±0.0002(16.6 ppm), calculated for $C_8H_7F_2O$ 157.04650 dev +0.0005(3.7 ppm).

Into a 70 ml glass tube, 0.02997g($1.11x10^{-3}$mole) of diphenylisobenzofuran was placed along with 4.3 mL of chloroform. The tube was then attached to a vacuum line by a rubber hose and the tube was placed in a dewar flask containing liquid N_2. The air was removed when the tube reached -198°C. Then 2.89g($3.12x10^{-3}$mole) of 1 was condensed into the tube, which was then sealed and allowed to react for 6 hours at 80°C. The reaction went to completion, observed by the loss of fluorescence when irradiated with UV light.

The product was obtained by evaporating off all volatile material under vacuum and purifying resultant solid by column chromatography. Yielding 0.357g(89%) of 106: ^{1}H NMR(100 MHz, $CDCl_3$) 8.0-9.0(CH, complex multiplet, 14 H), 2.7-2.6(CH_2, complex multiplet, 2H), 1.38-1.18(CH_2, complex multiplet, 2H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=133.58 ppm (mid-point), AB with further splitting, $\Delta\nu$=947.3 Hz; ^{13}C NMR (100 MHz, $CDCl_3$), decoupled, 128.5-127.1(aromatic), 88.96 (C_1,s), 119.4(C_2,s), 119.3(C_3,s), 87.6(C_4,s), 42.34(C_5,s), 41.3(C_6,t,$^{2}J_{CF}$=11.1 Hz), 123.3(C_7,t,J_{CF}=291.5 Hz), 18.53 (C_8,t,$^{2}J_{CF}$=10.01 Hz); IR($CDCl_3$), 3070, 3040, 2965, 1610, 1461, 1450, 1371, 1314, 1270, 1165, 1117, 1095, 983, 699 cm^{-1}; Mass spectrum gave M^{+} 366.1231$\pm$.0025(7 ppm), calculated for $C_{24}H_{18}F_2O$ 366.1232 dev .00016(.04 ppm).

1,1-Difluorospiro[2.4]hept-2-ene 107

The same sealed tube procedure used in the cyclopentadiene reaction is used here. Thus 0.12g($1.86x10^{-3}$mole) of butadiene and 0.086g($9.3x10^{-4}$mole) of 1 were placed in an evacuated glass tube. The sealed tube was then allowed to react for seven days at 110°C. Separation was achieved using a ¼"x20' DNP column(60mL/min, He), Tc=120°C. The retention time was 6.2 minutes, to give 0.0846g(63%) of 107: ^{1}H NMR(100 MHz, $CDCl_3$)δ5.75(CH, complex doublet, 2H), 2.27-1.98(CH_2, complex multiplet, 4H), 1.75(CH_2, doublet of doublets, 2H), 1.04(CH_2, complex doublet, 2H); ^{19}F NMR (100 MHz, $CDCl_3$), ϕ=98.4 ppm (mid point), AB with further

splitting, J_{ab}=152.5 Hz, $\Delta\nu_{ab}$=1439.95 Hz; IR(neat), 1475, 1200, 1010, 960, 900, 700, 650 cm^{-1}; Mass spectrum gave M^+ 144.0756±0.0021(15 ppm), calculated for $C_8H_{10}F_2$ 144.0700 dev -.0006(4.4 ppm).

5,5-Dichloro-1,1,3,3-tetrafluorospiro[2.3]hexane

Thus 0.1026g($1.14x10^{-3}$mole) of 2,2-difluoromethylene-cyclopropane was condensed into an evacuated tube along with 0.300g($2.28x10^{-3}$mole) of 1,1-dichloro-2,2-difluoro-ethylene and allowed to react for five days at 140°C. Separation was accomplished by a ¼"x10' 20% SE-30 column (68mL/min, He), Tc=85°C. The retention time was 15 minutes. Thus 0.0928g(21.8%) of the [2+2] cycloadduct was collected and identified as 108. ^1H NMR(100 MHz, $CDCl_3$)δ3.2(CH_2, complex multiplet, 1H), 2.68(CH_2, heptett, 1H), 2.02 (CH_2, heptett, 1H), 1.62(CH_2, complex multiplet, 1H); ^{19}F NMR (100 MHz, $CDCl_3$), ϕ=100.79 ppm(cyclobutyl fluorine mid-point), ϕ=139.44 ppm(cyclopropyl fluorine midpoint), both have AB pattern with further splitting, cyclobutyl J_{ab}= 515.2 Hz, $\Delta\nu_{ab}$=2466.32 Hz, cyclopropyl J_{ab}=264.5 Hz, $\Delta\nu_{ab}$=1643.2 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ(C_1, t, $^2J_{CF}$=28.12 Hz), 115.2(C_2,t,J_{CF}=296.18 Hz), 35.4(C_3, complex multiplet), 37.4(C_4,t,$^2J_{CF}$=24.3 Hz), 20.7(C_5,t, $^2J_{CF}$=10.24), 111.5(C_6,t,J_{CF}=288.7 Hz); IR(neat), 1485, 1395, 1300, 1250, 1220, 1000, 980, 910, 900, 825 cm^{-1}; Mass spectrum gave M-20 201.958±.0032(±16 ppm), calculated for $C_6H_3F_3Cl_2$ 201.960,dev .0016(+8.2 ppm).

4,4-Difluoro-5-vinylspiro[2.3]hexane

Again using the same sealed tube technique as above 0.104g($1.15x10^{-3}$mole) of difluoromethylenecyclopropane was condensed in an evacuated tube along with 0.115g ($2.12x10^{-3}$mole) of butadiene. The tube was sealed than allowed to react for 7 days at 110°C. Separation of the reaction mixture was accomplished using a ¼"x20' 20% TCP column(65mL/min, He), Tc=120°C, the retention time was 14 minutes for 109. Thus 0.069g(41.5%) of the [2+2] cycloproduct was collected and identified as ^{1}H NMR(100 MHz, $CDCl_3$),δ6.0(CH, complex multiplet, 1H), 5.2(CH_2, multiplet, 2H), 3.5(CH, multiplet, 1H), 2.1(CH_2, complex doublet, 2H), 1.0(CH_2 doublet of doublets, 2H), .7(CH_2, broad singlet, 2H); ^{19}F NMR(100 MHz, $CDCl_3$), ϕ= 102.37 ppm midpoint), AB with further splitting, J_{ab}= 187.06 MHz, $\Delta\nu_{ab}$=1574.78 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ117(C_1,s), 133(C_2,s), 48.7(C_3,t,$^{2}J_{CF}$=22.63 Hz), 124.2(C_4,t,J_{CF}=279.15 Hz), 27.16(C_5,t,$^{2}J_{CF}$=7.1 Hz), 28.39 (C_6,s), 9.59(C_7,s), 8.5(C_8,s); IR(neat) 660, 705, 910, 970, 1000, 1200, 1475 cm^{-1}; Mass spectrum gave M^{+}=144.0693± .0012(8.32 ppm), calculated for $C_8H_{10}F_2$ 144.070 dev +.0007 (.5 ppm)

5,5-Dichloro-4,4,6,6-tetrafluorospiro[2.3]hexane

Into an evacuated glass tube 0.1026g($1.14x10^{-3}$mole) of 1 was condensed along with 0.300g($2.28x10^{-3}$mole) of 1,1-dichloro-2,2-difluoroethylene. This reaction was allowed

to react for 4 days at 115°C. Separation was achieved by a ¼"x20' TCP column(60mL/min, He), Tc=110°C. The retention time was 12.5 minutes for the [2+2] adduct. Thus 0.115g($5.1x10^{-4}$mole, 44.9%) was collected and identified as 110: ^{1}H NMR(100 MHz, $CDCl_3$) 1.8(CH_2, singlet, 4H); ^{19}F NMR(100 MHz, $CDCl_3$) ϕ= 107.06 ppm, singlet; IR($CDCl_3$) 1380, 1310, 1190, 900, 730, 650 cm^{-1}.

cis-1,2-Dimethyl-3,3,4,4-tetrafluorocyclobutane and trans-1,2-dimethyl-3,3,4,4-tetrafluorocyclobutane 8 and 9

A five hundred mL autoclave was charged with 48.9g (.87 mole) of cis-2-butene and 44.2g(.442)moles) of tetrafluoroethylene. The autoclave was then placed in a bomb rocker and this mixture was then heated at 195°C for 24 hours. Pressures up to 2,000 lb/in^2 were observed. The autoclave was then cooled to room temperature and opened to a dry ice trap, which was connected to a drying tower. After the autoclave pressure was close to atmospheric, but slightly greater, the bomb was closed and then connected to a vacuum line. The bomb was then reopened and its contents transferred to a 200 mL round bottom flask equipped with a magnetic stirring bar. The round bottom flask was disconnected form the line and quickly stoppered and then connected to a distillation apparatus which was attached to a dry ice trap equipped with a drying tower. The flask was then allowed to warm to room temperature with stirring. The resultant mixture was transferred after an hour at

room temperature on the vacuum line into another smaller round bottom flask which upon disconnecting was stoppered with a rubber septum. The mixture was then separated by glpc using a ¼"x20' 20% TCP column(68mL/min, He, Tc=80°C, Ti=180°C, td=150°C). The retention times for the trans and cis isomers were 15 and 18 minutes respectively.

Then 6.2g(9%) of the first peak was collected and identified as trans-1,2-dimethyl-3,3,4,4-tetrafluorocyclobutane ^{1}H NMR(100 MHz, $CDCl_3$)δ2.38-2.01(CH, broad multiplet, 2H), 1.18-1.01(CH_3, doublet, 6H); ^{19}F NMR(100 MHz, $CDCl_3$) ϕ=123.89 ppm (midpoint), AB with further splitting, J_{ab}= 197.9 Hz, $\Delta\nu_{ab}$=2175.6 Hz IR($CDCl_3$) 3000, 1450, 1390, 1195, 1150, 1000, 900, 720 cm^{-1}; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ42.93-42.1(C_1,s complex multiplet), 122.4-114.0(C_3,C_4, doublet of virtual triplets, J_{CF}=278.74 Hz, $^{2}J_{CF}$=25.7 Hz), 10.4(C_5,C_6,s); Mass spectrum gave M^+ 156.0543± 0019(12.3 ppm), calculated for $C_6H_8F_4$ 156.0562 dev -.0018(11.8 ppm).

Also 2.1g 3,1%) of cis-1,2 dimethyl-3,3,4,4-tetrafluorocyclobutane was also collected: ^{1}H NMR(100 MHz, $CDCl_3$) δ2.95-2.53(CH, broad multiplet, 2H), 1.18-1.01(CH_3, doublet, 6H); ^{19}F NMR(100 MHz, $CDCl_3$)ϕ=123.46 ppm (midpoint), AB with further splitting, J_{ab}=185.9 Hz, $\Delta\nu_{ab}$=2159.6 Hz; ^{13}C NMR(100 MHz, $CDCl_3$), decoupled, δ123.15-114(C_3,C_4, doublet of doublet of virtual triplets, J_{CF}=292.6 Hz, $^{2}J_{CF}$=25.4 Hz; 38.2-37.3(C_1,C_2, complex multiplet), 6.1-6 (C_5,C_6 singlet). Mass spectrum gave M^+ 156.0552±.0017

(12 ppm), calculated for $C_6H_8F_4$ 156.0562 dev -.001(6.4 ppm) IR($CDCl_3$), 2995, 1450, 1390, 1200, 1160, 910, 730 cm^{-1}

Eighty torr of trans-1,2-dimethyl-3,3,4,4-tetrafluorocyclobutane was placed in an evacuated glass reaction vessel, which was submerged in a molten salt bath at 400°C. This was allowed to react for 24 hours. A sample of this reaction mixture was condensed and collected in a glass vessel and a GC-mass spectrum was run. The results showed no peaks at near the M^+ of either 2-butene or tetrafluoroethylene, the products of the unsymmetrical cleavage. Also the parent peak is identical to parent peak of difluoropropylene. The remaining mixture was condensed in an NMR tube and the ^1H NMR and ^{19}F NMR were recorded. The ^1H NMR and ^{19}F NMR were consistent with the reported values for difluoropropylene.

Kinetic Run

A storage bulb containing GC pure cis-1,2-dimethyl-3,3,4,4-tetrafluorocyclobutane was connected to the kinetic line, which had been evacuated. The well-conditioned reaction vessel, which is submerged in the molten salt bath, was also evacuated and its stopcocks closed. To insure that no air is ever exposed to the reaction vessel walls, the sample was degassed by a two freeze-degas-melt cycle. The pressure after this cycle was completed was less than

$5x10^{-2}$ torr, as measure by a Pirani gauge. Only after this condition was met was the sample allowed to warm and fill the vacuum lione which included a sampling bulb. At a pressure of 25 torr the stopcock to the storage bulb was closed and that of the reaction vessel opened and then quickly closed. The pressure was seen to reduce to 20 torr. The stopcock to the sampling bulb was closed. The timer was started at the time of the opening of the reaction vessel. The remaining contents in the vacuum line were condensed back into the storage bulb, which was at -196°C. The stopcock to the storage bulb was then closed along with the stopcock connecting the bulb to the line. The bulb was then removed. The line was then filled with argon up to 700 torr. The sampling bulb's stopcock was open and quickly closed. The sampling bulb was then removed from the line and another bulb was put in its place for another sample. The filled sampling bulb was attached to the gas injector port on the gas chromatograph. The gas injector port has an opening to vacuum pump thus allowing the removal of air before injecting. After this was done, the port was closed to the vacuum pump and the sampling bulb was opened and then closed. The port was once again evacuated and filled before the injection was made. The results from this injection gave the initial concentrations. To obtain other readings the sampling area is closed off from the rest of the line and the reaction vessel is

opened and then quickly closed. The sampling bulb, which is evacuated, is closed prior to filling the sampling area. The line is filled with Argon and the stopcock to the sampling area is open and then quickly closed. After the gases have equilibrated, the sampling bulb is opened and then closed. This bulb is now ready for injection. Of course the time was recorded at the moment the reaction vessels stopcock was opened. The assumption that difluoropropene had exactly one-half the detector response of the cyclobutane was tested by an internal standard, pentane. The pentane concentration did not change with time. This was interpreted as proof that difluoropropense response was one-half that of the cyclobutanes because a change in pentane concentration is expected if this were not true. The concentration would increase if there was a detector response less than one-half and decrease if the detector response was greater.

APPENDIX: A DISCUSSION OF SIMPLEX PROGRAM

In this section a complete discussion of the simplex program for the kinetic scheme used in the interpretation of the data will be presented. Simplex is a method of optimization of a best guess. Thus in order to use this program efficiently a fairly good guess should be made. Note a bad guess can be used but the chance of error increases and computer time soars. To obtain a good guess, a program, "Approx" was used. This program shown below generates the

```
10 DISP "APPROX"
20 DISP "RATE CONSTANTS"
30 INPUT W.X.Y.Z.
40 A=1
50 B=0
60 C=0
70 S=W+Y
80 T=X+Z
90 Q=(S+T)/2+SQR((S-T)^2/4+W*X)
100 R=(S+T)/2-SQR((S-T)^2/4+W*X)
110 L=X/(T-Q)
120 M=X/(T-R)
130 N=S-W*L
140 O=S-W*M
150 E=0
160 A=1-1/(L-M)*(L*N/R*(EXP(-Q*E)-1)-L*O/R*CEXP(-R*E)
    -1))
170 B=1/(L-M)*(N/Q*(EXP(-Q*E)-1)-O/R*(EXP(-R*E)-1))
```

```
180 C=1/(L-M)*((M-1)*(N/Q)*(EXP(-Q*E)-1)-(L-1)*
    (EXP(-R*E)-1))
190 A=1-(B+C)
200 DISP A,B,C,E
210 E=3600+E
220 IF E<259201 THEN 170
230 END
```

concentrations of A, B and C at any time E. The input is the four rate constants. Thus by placing in four rate constants in the order k_1, k_{-1}, k_2, k_3 and choosing a similar time interval as the experimental, one can obtain the concentrations of A, B and C at a different time E. By comparing the computer results with the experimental a better guess can be made. The first set of our rate constants are the most difficult. The third set of rate constants can be obtained by the Arrhenius equation. Once a good approximation between the results of these calculation and the experimental data is made so the simplex program is ready to be used.

How to Run the Simplex Program

After the program has been placed in computer memory hit the run button. A list of instructions will be printed out. The program will stop and the last statement will read "Enter Concentrations of A, B, C. Enter your first data points for A, B and C, which are 1,0,0, then hit return. The statement "Enter time T" will appear. Type in initial

data point for time T, which is 0. Again the program will ask for the concentration of A, B and C until all the data has been entered. At this point the concentrations of -1,-1,-1 are entered. The command "Enter best guesses of K_1, K_2, K_3 and K_4" will appear. After these have been entered, the program will run until the optimal values of k_1, k_2, k_3 and k_4 have been obtained.

Line by Line Description

A description of the line by line computations is given below. This should prove very helpful to any debugging attempt made by future users.

10-90 Introductory remarks and instructions on how to run the program

100 Dimensioning of arrays; V(9,4) is the array in which 9 sets of 4 rate constants are stored, W(4) and U(4) are the upper and lower constraints respectively, K(4) is the final print out of the four rate constants, R(3), D(10), M(3), and S(2) are arrays for the simplex variables. T(12), L(12), and Z(12) are the arrays for the print out of the deviation between experimental and calculated results. 6(9,4) is an array for the storage of the experimental concentrations of A, B, C, and time. A(10), B(10) and E(10) are the arrays for the calculated concentrations of A, B and C respectively.

120 The initial conditions are placed in this line.

130-180 These lines are the input statements for experimental data.

190 This line is for the input of the best guesses for the four rate constants.

200-230 The determination of F upper and lower constraints is performed here. Note 20% + or - of the best guess can be changed by the user.

240 60 SUB 410 is the command which sends program to a subroutine starting with line number 410.

250-400 These lines are not used until the rate constant have been optimized. The commands are for a print out of experimental concentartions, the calculated concentration, and the deviation between these two concentrations.

410-670 These lines are responsible for the assignment of simplex variables and the generation of seven sets of four different rate constants. Thus seven different k_1, k_{-1}, k_2 and k_3 are obtained by multiplying a randomly generated variable to the upper and lower constraints.

680 Sends program to subprogram, "Approx", where the concentrations of A, b and C are calculated, compared to experimental data to calculate the square root of the sum of deviations squared shown below, for each set of rate constants generated.

$$S= \quad ([A]_{ex}-[A]_{cal})^2+ ([B]_{ex}-[B]_{cal})^2+ ([C_{ex}]-[C_{cal}])^2$$

690 The number of times the subprogram "Approx" is used is recorded.

700-710 A print out is made for the first eight sets of four rate constants, the rate constants row number in array and the value of S. This was done to ensure the program was running to this point.

720 A display is made each time a new set is generated. This is the only evidence that the program is running. Each new display shows; the set number 1 to 8 that was the number of the previous set of rate constants that yielded the highest value of S, the value of S, for the new set and the lowest value of S thus far generated by one of the eight sets of rate constants. For each new display a lower S value should be observed and a different set number. If this is not the case, than an error in the program exists.

730-750 The set of rate constant that yielded the lowest S value is assigned by the program as the best set so far.

760-790 The set of rate constants that are responsible for the highest value of S are identified and defined.

800 This set is shown in the display.

810-840 These lines rename the set of rate constant that caused the highest value, so that another new set can be generated.

850-860 The program is told to leave this subroutine if the difference between the highest S value and lowest S value is less than $1x10^{-6}$.

870-880 If the new set of rate constant does not yield a lower S value the program is sent to line 1050.

890-950 Four new rate constants are generated here. The new rate constants are derived from an equation based on the average of all the other seven rate constants.

970-1020 The new rate constants are checked to insure they lie within the constraints.

1030 A display of the new rate constants is the call for.

1040 The program is sent to line 1140

1050-1070 The program was sent here from line 870, this is the only entrance into these lines. The condition for entrance is the program was unable to generate a new set of rate constants in line 890-950 which yielded a lower S value than the previous highest S value. Thus four new rate constants are calculated based on the average of the other seven rate constants and on the rate constants yielding the lowest S value.

1080-1130 The new rate constants are checked with th~ constraints.

1140 The program is sent to the subprogram "Approx".

1150 The number of times "Approx" is called is recorded here.

1160 The S value of the new rate constant is checked with the highest S value. If it is less than, the process will begin aga'n where the next highest S value will be removed and replaced by another set of rate constants that give a lower S value. If the S value of the new set is greater than the highest S value then the program is sent to line 1170.

1170 If this is the first time the new set was unable to get a lower S value the program is sent to line 1180. If it is second time, the program was unable to get a lower value of S, the program will be sent to line 1230.

1180-1220 The new rate constants which yielded a higher S value after one attempt, are placed in the array of rate constant where it will not be used for the calculation and the program is sent to line 1050.

1230-1430 The condition for the use of this section of the program is only in the rare case that the program was unable to generate four rate constants which yielded an S value lower than the highest

```
1800 DISP "K(1)="; K(1)
1810 DISP "K(2)="; K(2)
1820 DISP "K(3)="; K(3)
1830 DISP "K(4)="; K(4)
1840 S=O
1850 S(1)=K(1)+K(3)
1860 S(2)=K(2)+K(4)
1870 T(1)=(S(1)+S(2))/2+SQR((S(1)-S(2)) 2/4+K(1)*K(2))
1880 T(2)=(S(1)+S(2))/2-SQR((S(1)-S(2)) 2/4+K(1)*K(2))
1890 L(1)=K(2)/(S(2)-T(1))
1900 L(2)=K(2)/(S(2)-T(2))
1910 Z(1)=S(1)-K(1)*L(1)
1920 Z(2)=S(1)-K(1)*L(2)
1930 FOR I-1 TO P
1940 X(I)=EXP(-T(1)*G(I,3))-1
1950 Y(I)=EXP(-T(2)*G(I,3))-1
1960 A(I)=1-1/L(1)-L(2))*(L(2)*Z(1)/T(1)*X(I)-L(1)&Z(2)*
     Y(I)/T(2))
1970 B(I)=1/(L(1)-L(2))*Z(1)*X(I)/T(1)-Z(2)*Y(I)/T(2))
1980 E(I)=1/(L(1)-L(2))*((L(2)-1)*Z(1)*X(I)/T(1)-(L(1)-1)*
     Z(2)*Y(I)/T(2))
1990 S=S+(A(I)-G(I,1)) 2+(B(I)-G(I,2)) 2+(E(I)-G(I,4))
2000 NEXT I
2010 F(N)=S
2020 RETURN
2030 END
```

S value calculated by two different methods. The program now will generate eight new sets of rate constants. After each new set the program is sent to the subprogram "approx".

1440-1450 The S value for the new set of rate constants is checked against the lowest S value if the new S value is greater than the lowest S, then the program is sent to line 1660. If the new set yields a new lowest S value then the program goes to line 1470.

1460 The program will stop after the subroutine is called 300 times. This line was placed in there to make sure the program did not run indefinitely.

1470 The new lowest S value yielding rate constants are defined as such.

1480-1520 A new set of rate constants are calculated based on the new lowest S value.

1530-1570 These new rate constants are checked against the constraints.

1580-1590 The program is sent to subroutine "Approx" and the number of times this has occurred is counted.

1600-1660 Again the new S value is checked against the lowest S value.

1670-1730 This section of the program will be entered only when Z from line 860 is less than $1x10^{-6}$ or when the subprogram has been entered 300 times.

The program will print out all values for the eight set of four rate constants and return the program to line 250.

1750-1980 This section of the program is the subroutine "Approx". The concentration of A, B and C are calculated for any time, t.

1990-2010 The calculation of the value of S is performed by this line.

2020 This line returns the program back to the line which called this subroutine.

2030 The End.

APPENDIX: B SIMPLEX PROGRAM

```
10 DISP "IMPROVE"
20 DISP "THIS PROGRAM IS DESIGNED TO GIVE THE BEST
   APPROXIMATION OF RATE CONSTANT FOR THE"
30 DISP "KINETIC SCHEME WHERE A IS IN EQUILIBRIUM WITH B
   AND BOTH A AND B GO TO C"
40 DISP "THE INPUT WILL BE THE CONCENTRATIONS OF A, B, +C
   AT A TIME T"
50 DISP "AFTER THIS ONE MUST TYPE IN A BEST GUESS OF THE
   RATE CONSTANTS K1, K2, K3, and K4"
60 DISP "THESE MAY BE OBTAINED FROM THE PROGRAM APPROX"
70 DISP "WHEN ALL OF YOUR DATA POINTS HAVE BEEN ENTERED,
   ENTER A DATA POINT OF -1 FOR A, B, C."
80 DISP "AFTER THIS ONE MUST TYPE IN THE BEST APPROXIMATIONS
   OF K1, K2, K3, K4 THESE MAY BE OBTAINED"
90 DISP "FROM THE PROGRAM APPROX"
100 DIM V(9,4),W(4),U(4),K(4),S(2),T(2),L(12),Z(12),X(9),
    Y(9),A(10),G(9,4),B(10),E(10)
110 DIM R(3),C(10),M(3),D(10)
120 A=1 & B=0 & C=0 & P=0
130 FOR I=1 TO 10
140 DISP "ENTER CONCENTRATIONS OF A,B,C" & INPUT G(I,1),
    G(I,2),G(I,4)
150 IF G(I,1)=-1 THEN 190
160 DISP "ENTER TIME T" & INPUT G(I,3)
170 P=P+1
180 NEXT I
```

```
190 DISP "ENTER BEST GUESS OF K1,K2,K3,K4" & INPUT V(1,1),
    V(1,2),V(1,3),V(1,4)
200 FOR J=1 TO 4
210 W(J)=V(1,J)+ 2*V(1,J)
220 U(J)=V(1,J)- 2*V(1,J)
230 NEXT J
240 GO SUB 410
250 DISP "AC"; "AX"; "BC"; "BX"
260 FOR I=1 TO P
270 T(I+2)=G(I,1)-A(I)
280 L(I+2)=G(I,2)-B(I)
290 Z(I+2)=G(I,4)-E(I)
300 PRINT "EXP"; "CAL"; "DEV"
310 PRINT G(I,1); A(I); T(I+2)
320 PRINT G(I,2); B(I); L(I+2)
330 PRINT G(I,4); E(I); Z(I+2)
340 NEXT 1
350 PRINT "K(1)="; K(1)/3600
360 PRINT "K(2)="; K(2)/3600
370 PRINT "K(3)="; K(3)/3600
380 PRINT "K(4)="; K(4)/3600
390 DISP K(1), K(2), K(3), K(4)
400 END
410 C(6)=O
420 C(1)=1
430 RANDOMIZE .0000002
440 C(2)=O
```

```
450 C(3)=2
460 C(4)=C(3)-1
470 M(1)=9
480 N=O
490 C(5)=1
500 M(2)=O
510 GO SUB 1750
520 C(6)=C(6)+1
530 PRINT N; F(N); V(N,1); V(N,2); V(N,3); V(N,4)
540 FOR N=2 TO 8
550 M(3)=N-1
560 FOR K=1 TO 4
570 D=O
580 FOR J=1 to M(3)
590 D=D+V(J,K)
600 NEXT J
610 D(K)=D/M(3)
620 L=RND
630 R(2)=L
640 R(3) = ABS(RND-R(2))/5
650 L=R(3)-.0000001*R(2)
660 V(N,K)=R(3)*(W(K)-U(K)+U(K))
670 NEXT K
680 GO SUB 1750
690 C(6)=C(6)+1
700 IF C(6)>8 THEN 720
710 PRINT N;F(N); V(N,1); V(N,2); V(N,3); V(N,4)
```

```
720 DISP N; F(N); F(C(5))
730 IF F(C(5))-F(N)<O THEN 750
740 C(5) = N
750 NEXT N
760 LET N=1
770 FOR J=2 TO 8
780 IF F(N)-F(J)<O THEN N=J
790 NEXT J
800 DISP N; F(N)
810 FOR j=1 TO 4
820 V(M(1),J)=V(N,J)
830 NEXT J
840 H=F(N)
850 Z=.0000001
860 IF Z-ABS(F(C(5))-F(N))>O THEN 1670
870 IF N-M(2)=O THEN 1050
880 M(2)=N
890 FOR k=1 TO 4
900 D=O
910 FOR J=1 TO 8
920 D=D+V(J,K)
930 D(K)=(D-V(N,K))/M(3)
940 NEXT J
950 V=2*D(K)-1*V(N,K)
960 IF V>U(K) THEN 990
970 V=U(K)
980 GO TO 1010
```

```
990 IF V<W(K) THEN 1010
1000 V=W(K)
1010 V(N,K)=V
1020 NEXT K
1030 DISP V(N,1); V(N,2); V(N,3); V(N,4); H; M(2)
1040 GO TO 1140
1050 M(2)=O
1060 FOR J=1 TO 4
1070 V=.5*(D(J)+V(C(5),J))
1080 IF V U(J) THEN 1100
1090 V=U(J)
1100 IF V>W(J) THEN 1120
1110 V=W(J)
1120 V(N,J)=V
1130 NEXT J
1140 GO SUB 1750
1150 C(6)=C(6)+1
1160 IF H-F(N)>=O THEN 1450
1170 IF M(2)=O THEN 1230
1180 FOR I=1 TO 4
1190 V(N,I)=V(M(1),I)
1200 NEXT I
1210 F(N)=H
1220 IF C(6)<300 THEN 1050
1230 N=M(1)
1240 FOR K=1 TO 8
1250 IF K-C(5)=O THEN 1430
```

```
1260 FOR J=1 TO 4
1270 V=.5*(V(K,J)+V(C(5),J))
1280 IF V>U(J) THEN 1300
1290 V=U(J)
1300 IF V<W(J) THEN 1320
1310 V=W(J)
1320 V(N,J) =V
1330 NEXT J
1340 IF C(6)>300 THEN 1670
1350 GO SUB 1750
1360 C(6)=C(6)+1
1370 FOR J=1 TO 4
1380 V(K,J)=V(N,J)
1390 NEXT J
1400 F(K) = F(N)
1410 IF F(K)-F(C(5))>=0 THEN 1430
1420 C(5)=K
1430 NEXT K
1440 GO TO 1660
1450 IF F(C(5))-F(N)<=0 THEN 1660
1460 IF C(6)> 300 THEN 1670
1470 C(5)=N
1480 N=M(1)
1490 FOR K=1 TO 4
1500 V=C(3)*V(C(5),K)-D(K)
1510 IFV>U(K) THEN 1540
1520 V=U(K)
```

```
1530 GO TO 1560
1540 IF V<W(K) THEN 1560
1550 V=W(K)
1560 V(N,K)=V
1570 NEXT K
1580 GO SUB 1750
1590 C(6)=C(6)+1
1600 IF F(C(5))-F(N)<=0 THEN 1660
1610 FOR K=1 TO 4
1620 V(C(5),K)=V(N,K)
1630 NEXT K
1640 F(C(5))=F(N)
1650 N=C(5)
1660 IF C(6)<300 THEN 760
1670 PRINT C(6)
1680 FOR K=1 TO 8
1690 FOR J=1 TO 4
1700 PRINT K; F(K); V(K,J)
1710 NEXT J
1720 NEXT K
1730 RETURN
1740 END
1750 IF N=0 THEN N=1
1760 K(1)=V(N,1)
1770 K(2)=V(N,2)
1780 K(3)=V(N,3)
1790 K(4)=V(N,4)
```

APPENDIX: C COMPARISON OF COMPUTER AND EXPERIMENTAL DATA

T = 434.75°C

time(hr)	[A] Exp.	[A] Cal.	[A] Dev.	[B] Exp.	[B] Cal.	[B] Dev.	[C] Exp.	[C] Cal.	[C] Dev.
1.0	.7026	.7062	-.0036	.2607	.258	.002	.0366	.0351	.0015
2.03	.519	.5196	0.0006	.4162	.4154	.0007	.0648	.0649	-.00018
2.22	.3848	.3834	.0013	.5163	.5196	-.0033	.0989	.0968	-.00201
4.7	.3039	.3053	-.0014	.5712	.568	.003	.1248	.1265	0.0017
6.05	.2629	.2627	.0012	.582	.584	-.002	.154	.1532	.0008
8.0	.2318	.229	.00196	.584	.584	.003	.1842	.189	.005
11.03	.2014	.2048	-.0034	.5551	.554	.0007	.2436	.2408	.0027

T = 441°C

	[A]			[B]			[C]		
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.5	.7427	.7436	-.0009	.2256	.2241	.0014	.0317	.0322	-.0005
1.0	.5677	.5719	-.0042	.374	.3689	.005	.0604	.0591	.00128
1.52	.4569	.453	.0036	.4605	.4636	-.0032	.0826	.083	-.00047
2.07	.3754	.3698	.0055	.52	.5244	-.0044	.1046	.1056	-.001
3.05	.2809	.2852	-.0043	.5764	.5734	.003	.1428	.1414	.0014
4.17	.2394	.2392	.0002	.5834	.5832	.0002	.1771	.1776	-.0005
5.00	.2226	.2205	.002	.5761	.5766	-.0005	.2012	.2028	-.00163
6.00	.2039	.2060.	002	.5599	.5623	-.0024	.233	.232	.0013
8.00	.1848	.1875	-.0027	.5277	.5267	.001	.2842	.2852	-.0016

T = 444.7°C

time(hr)	[A] Exp.	[A] Cal.	[A] Dev.	[B] Exp.	[B] Cal.	[B] Dev.	[C] Exp.	[C] Cal.	[C] Dev.
.55	.7038	.7085	-.0047	.2578	.2537	.004	.0382	.0377	.0004
1.0	.5561	.5526	.0034	.3832	.3836	-.0004	.0606	.0636	-.003
1.5	.4416	.4361	.0054	.4734	.4750	-.0016	.085	.088	-.003
2.0	.3555	.3588	-.0033	.5335	.5296	.0038	.111	.1114	-.0004
2.5	.309	.3072	.002	.5593	.5605	-.0012	.1318	.1323	-.0005
4.03	.2247	.2296	-.0049	.582	.5811	.00089	.1932	.1892	.0039
5.00	.212	.208	.0036	.572	.5697	.0023	.216	.222	-.006
6.66	.1865	.1874	-.0023	.5357	.5380	-.0023	.28	.275	+.005

T = 450.2°C

	[A]			[B]			[C]		
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.33	.7452	.7450	.0002	.2203	.2236	-.0033	.0346	.0314	.0032
.68	.5729	.5628	.01	.3668	.3774	-.01	.0603	.0597	.0005
1.0	.4704	.4525	.0179	.4593	.4655	-.0062	.0799	.0820	-.00213
1.5	.3531	.3423	.0101	.5313	.5438	-.0125	.1156	.1131	.0024
2.0	.295	.280	.0145	.5661	.5785	-.0124	.1389	.141	-.0021
2.5	.2528	.2436	.009	.5822	.5895	-.0073	.165	.1668	-.002
3.83	.2063	.1987	.0075	.5625	.5717	-.0092	.2312	.2295	.0017

T - 461.3°C

	[A]			[B]			[C]	
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.25	.660	.6679	-.0079	.2928	.2876	.0052	.0472	.0444	.0028
.5	.481	.478	.0022	.4408	.4418	-.0010	.078	.0794	-.00138
1	.31	.306	.0039	.5577	.559	-.0013	.1318	.1348	-.00306
1.42	.216	.2137	.0023	.553	.556	-.003	.2309	.2300	.0008
2.67	.1935	.1972	-.0037	.531	.528	.003	.275	.2748	.00014
3.5	.1781	.1796	-.0015	.4866	.4853	.0013	.3334	.3352	-.0012
5.57	.1418	.1448	-.0032	.3897	.3925	-.0027	.4684	.4625	.058556
7.16	.1284	.1228	.0056	.3366	.3325	.004	.535	.545	.00

T = 467.25°C

	[A]			[B]			[C]		
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.2	.6309	.6266	.0043	.3182	.3167	.0015	.0508	.0566	.0058
.4	.4324	.4328	-.0004	.4712	.4686	.0026	.0964	.0986	-.0022
.5	.3761	.3738	.0023	.5091	.5098	-.0008	.1148	.1163	-.0015
1.0	.2454	.2438	.0016	.5694	.5668	.0026	.1852	.1894	-.0042
1.5	.2137	.2068	.0069	.5442	.5425	.0017	.2634	.2506	.0128
2.12	.1744	.1845	-.0100	.4972	.4971	.0012	.3283	.3185	.0098
2.72	.1648	.1678	-.0030	.4553	.4539	.0014	.3800	.3783	.0017
4.37	.1325	.1303	.0022	.3560	.3525	.0035	.5116	.5172	-.0056

T = 472.5°C

	[A]			[B]			[C]	
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.1	.7378	.7397	-.002	.228	.2255	.0245	.034	.0347	-.0007
.55	.304	.3014	.0027	.5588	.5575	.0013	.1373	.1411	-.004
1.0	.2194	.2183	.0011	.5634	.5632	.00023	.2172	.2186	-.0014
1.5	.1883	.1886	-.0003	.5179	.51798	-.00008	.2937	.2935	.00023
2.02	.1713	.1689	.002	.4695	.4682	.0013	.3592	.3629	-.0037
2.52	.15	.1527	-.0027	.4174	.4237	-.0064	.4376	.4235	.009
3.5	.1259	.1245	.0004	.3522	.3481	.004	.5219	.5264	-.0045

T = 479°C

	[A]			[B]			[C]		
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.1	.6414	.6428	-.0014	.3085	.3062	.0023	.0501	.0510	-.0009
.167	.5002	.5012	-.001	.4211	.4197	.0014	.0787	.0790	-.003
.25	.3958	.3896	.006	.4976	.500	-.003	.1066	.1094	-.0028
.5	.2566	.2505	.006	.5576	.563	-.006	.1859	.1860	-.0001
1.0	.1827	.1876	-.005	.5012	.5014	-.0002	.3158	.3109	.005
1.5	.1558	.582	-.002	.4328	.4263	.006	.4114	.4156	-.004
2.0	.1324	.1341	-.0017	.3598	.3616	-.0018	.5078	.5042	.0035
2.5	.1135	.1137	-.0002	.3073	.3067	.0005	.5791	.5794	-.00036

T = 483°C

	[A]			[B]			[C]		
time(hr)	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.	Exp.	Cal.	Dev.
.216	.3789	.3757	.0031	.5073	.5089	-.0016	.1138	.1154	-.0015
.417	.236	.2419	-.0060	.5621	.557	.0048	.2018	.2007	.0011
.667	.1931	.1917	.0018	.5151	.5155	-.0004	.2917	.2932	-.0016
1.0	.1606	.1590	.0016	.4340	.4416	-.0076	.4054	.3993	.0061
1.25	.1419	.1405	.0014	.3940	.3912	.0028	.4641	.4683	-.0042

APPENDIX: D IR and ^{1}H NMR SPECTRA

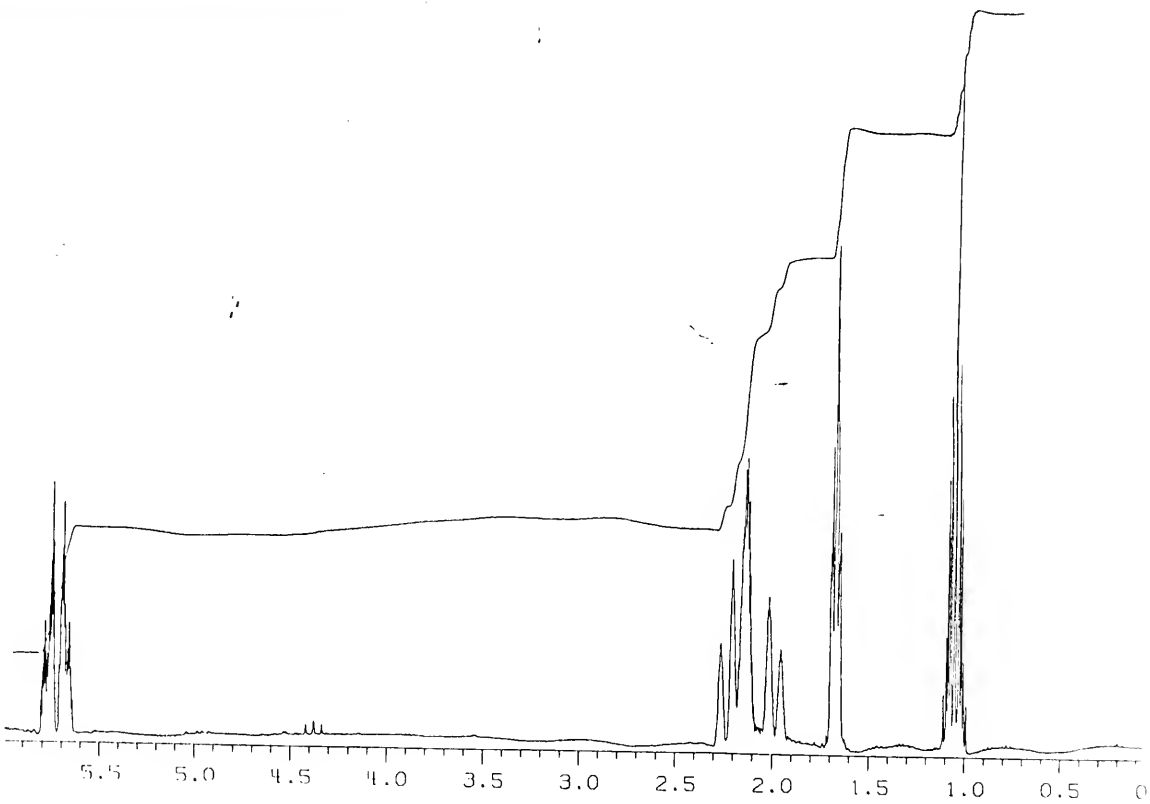


Figure 3. NMR ($CDCl_3$): Endo-1,1-diflurospiro[bicyclo[2.2.1]]-hept-2-ene-6.2'-cyclopropane 93.

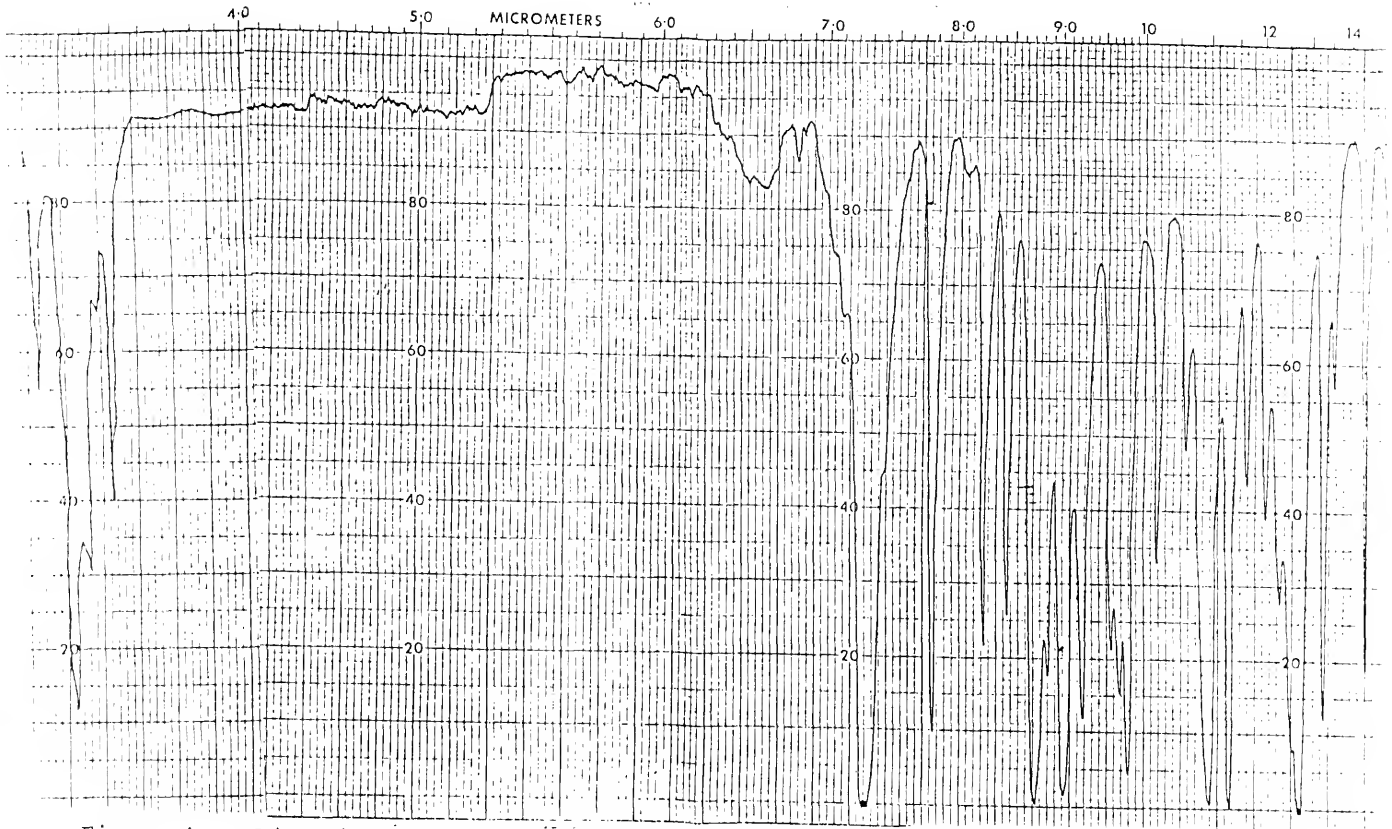


Figure 4. IR(Neat): Endo-1,1-difluorospiro[bicyclo[2.2.1]]-hept-2-ene-6.2'-cyclopropane 93.

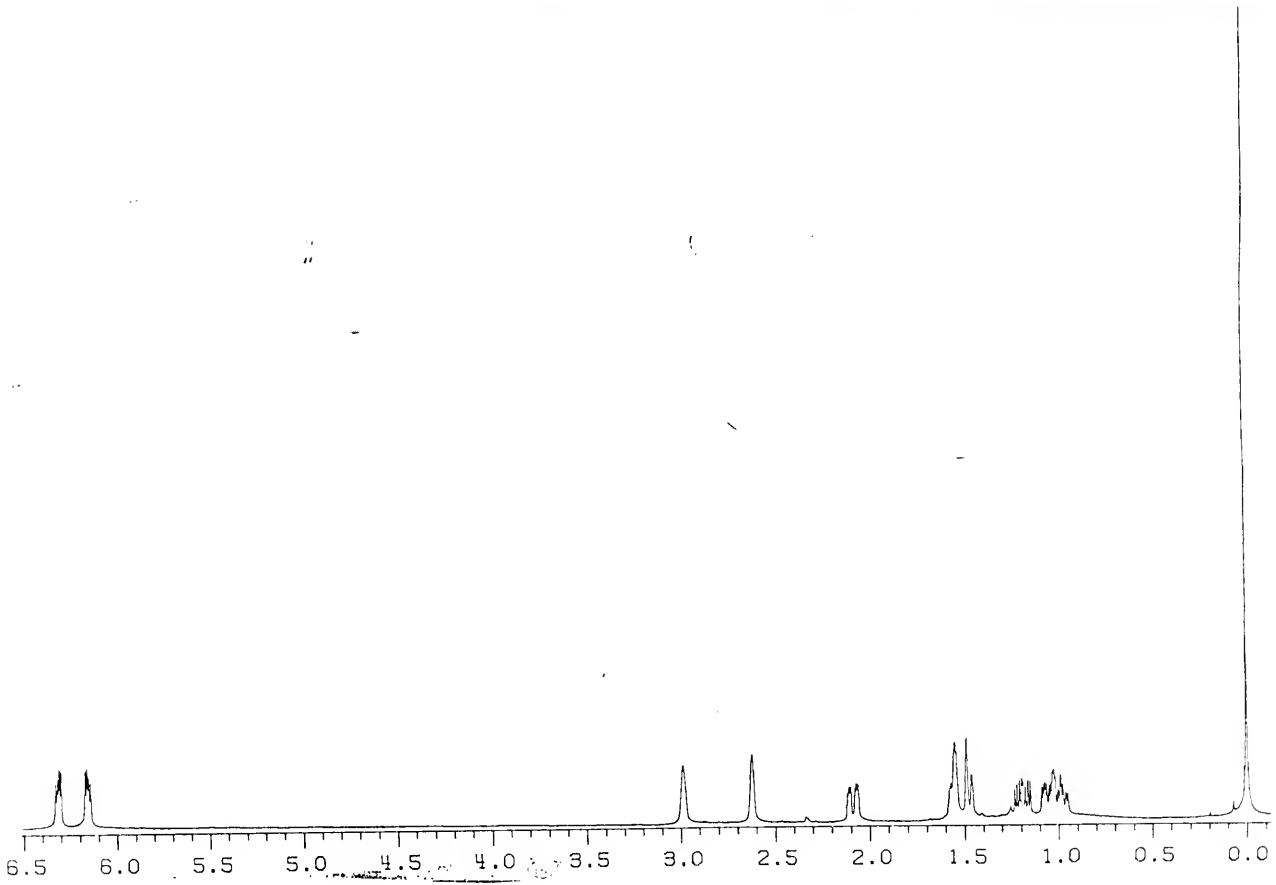


Figure 5. NMR ($CDCl_3$): Exo-1,1-diflurospiro[bicyclo[2.2.1]]-hept-2-3n3-6.2'-cyclopropane 94.

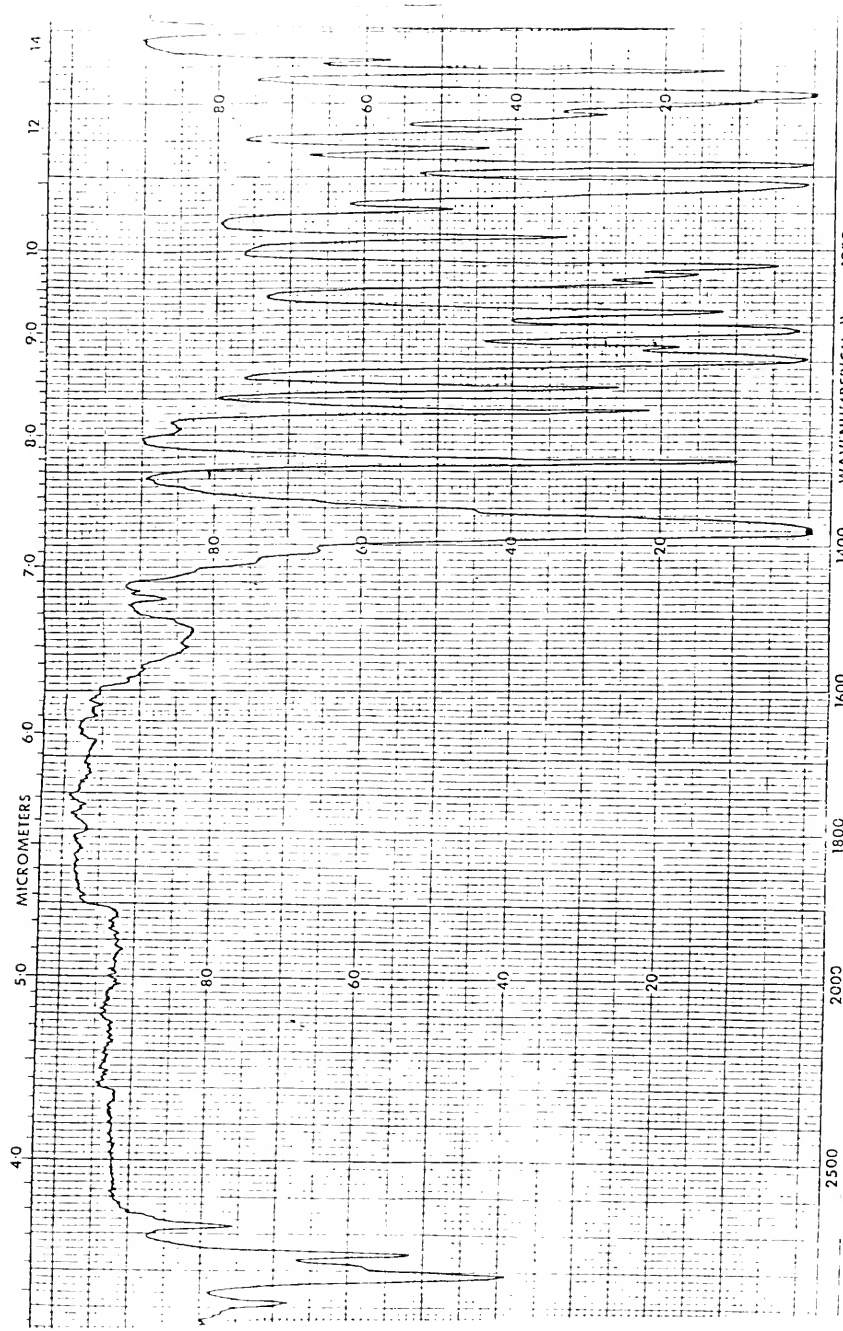


Figure 6. IR(Neat): Exo 1,1-difluorospiro[bicyclo[2.2.1]]-hept-2-ene-6,2'-cyclopropane 94.

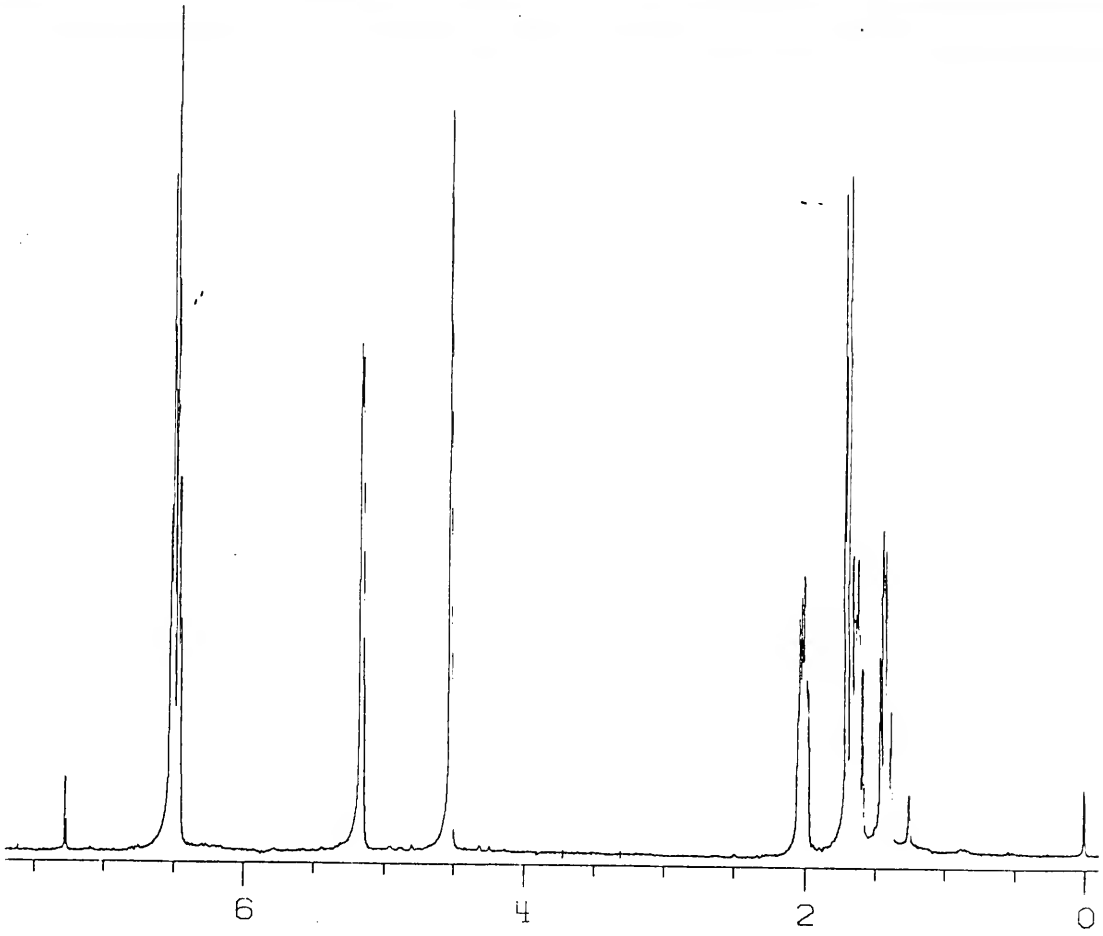


Figure 7. NMR ($CDCl_3$): Endo-1,1-difluorospiro[oxabicyclo[2.2.1]]-hexa-2-ene-6,2'cyclopropane 102.

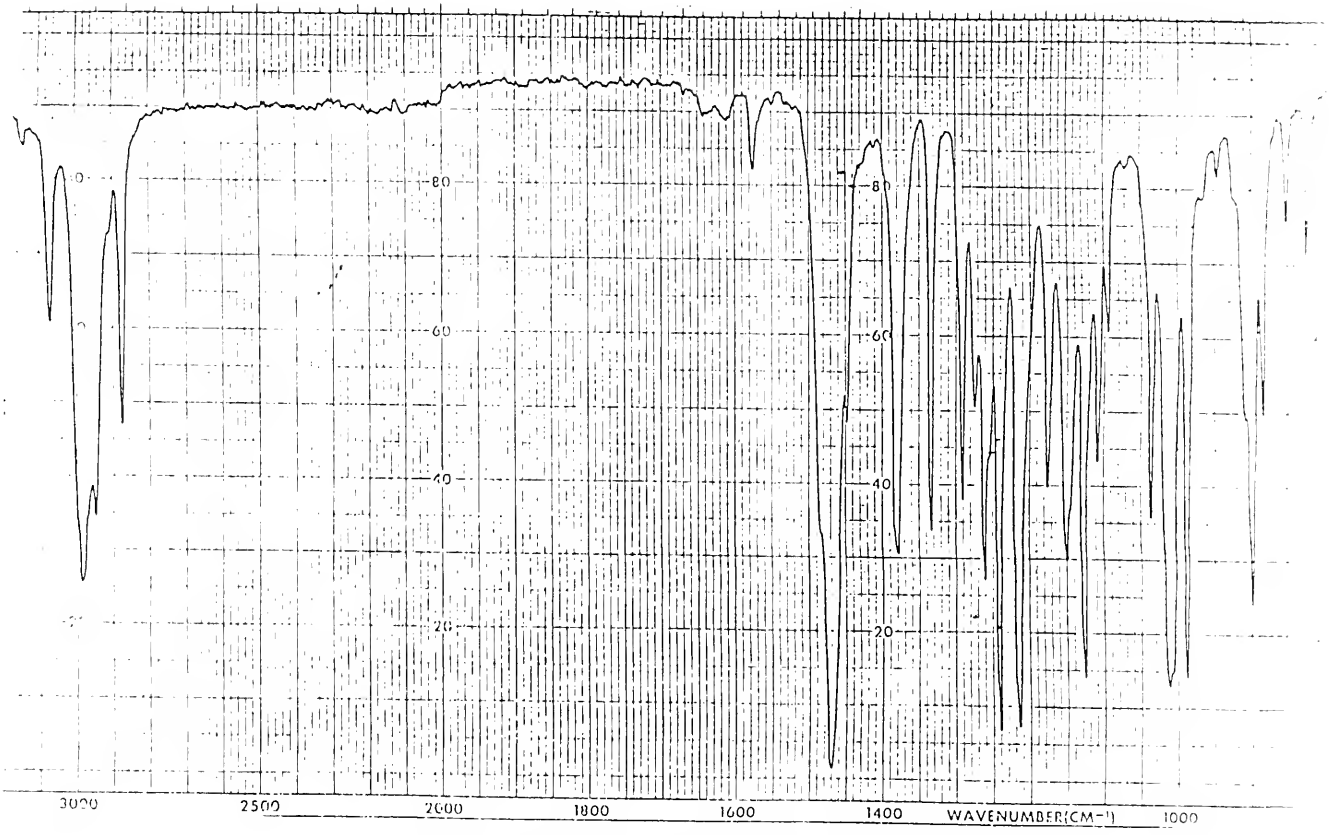


Figure 8. IR(Neat): Endo-1,1-difluorospiro[oxabicyclo[2.2.1]]-hexa-2-ene-6,2'cyclopropane 102.

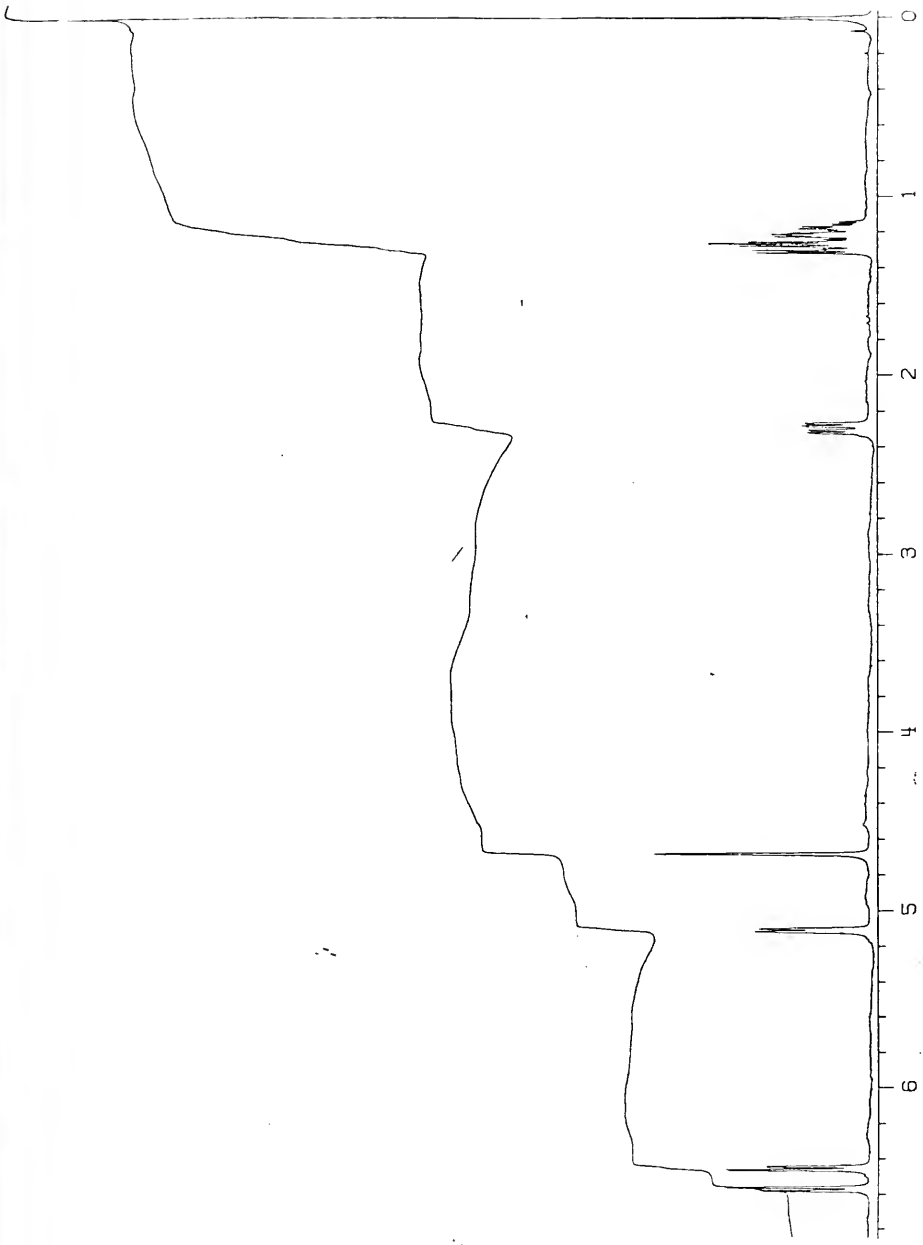


Figure 9. NMR ($CDCl_3$): Exo-1,1-difluorospiro[oxabicyclo[2.1.1]-hexa-2-ene-6,2' cyclopropane 103.

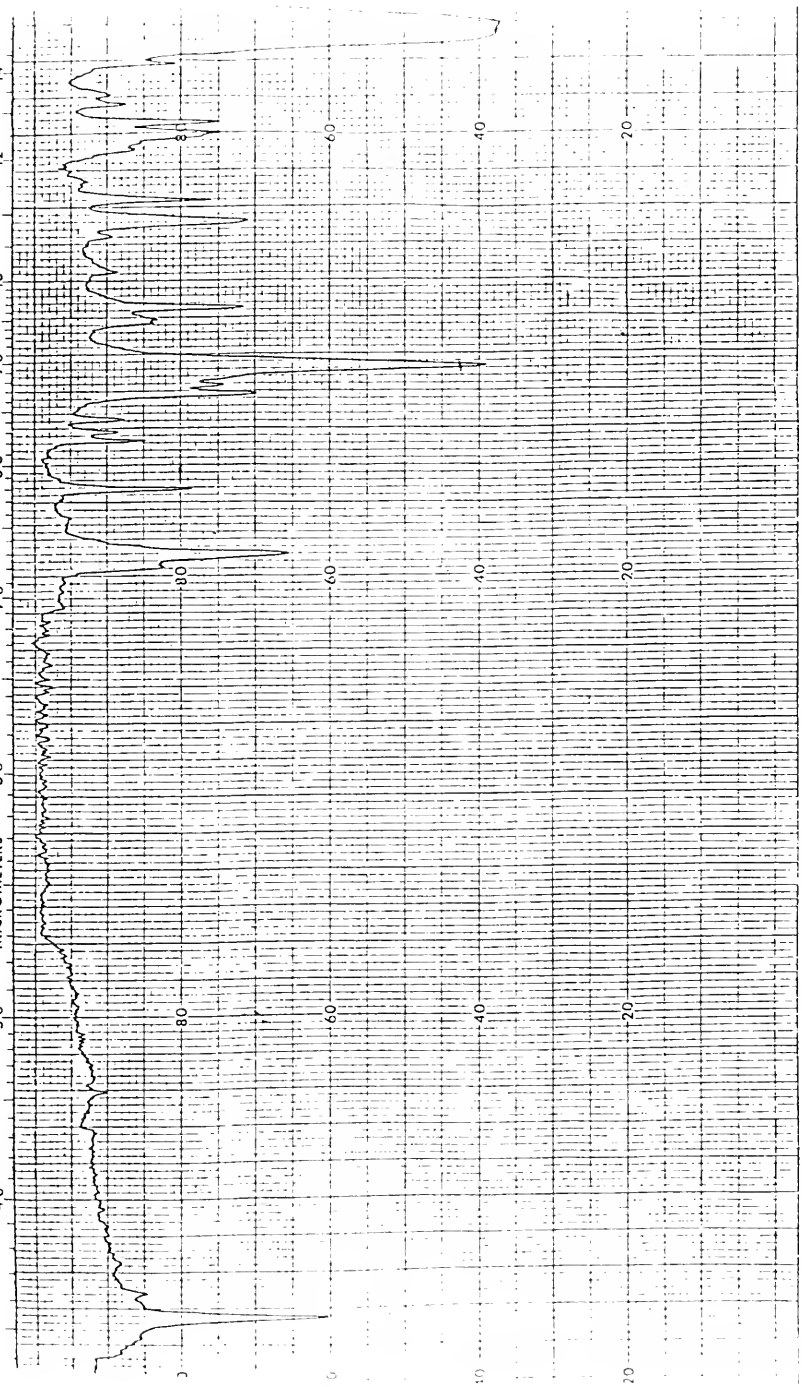


Figure 10. IR(Neat): Exo-1,1-difluorospiro[oxabicyclo[2.2.1]]-hexa-2-ene-6,2'cyclopropane 103.

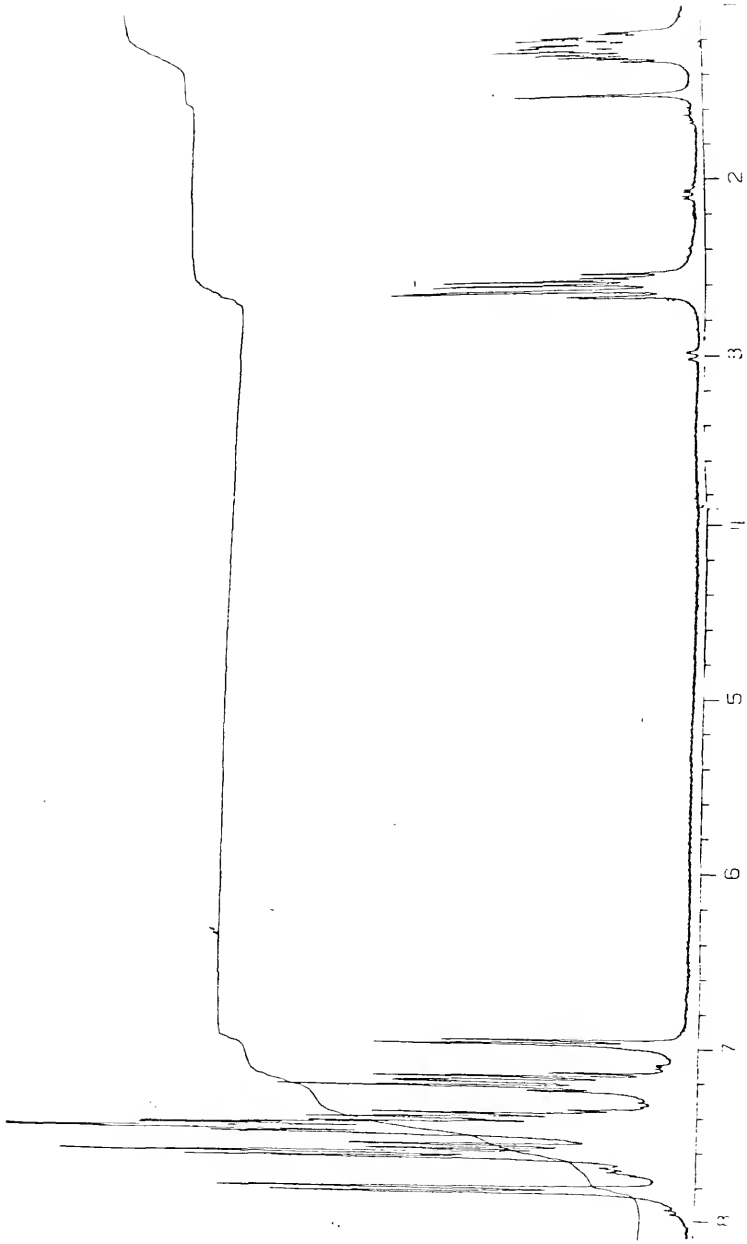


Figure 11. NMR ($CDCl_3$): Endo-1,1-difluorospira[oxabicyclo[2.2.1]]-4,7-epoxy-naphthalene-6,2'cyclopropane 106.

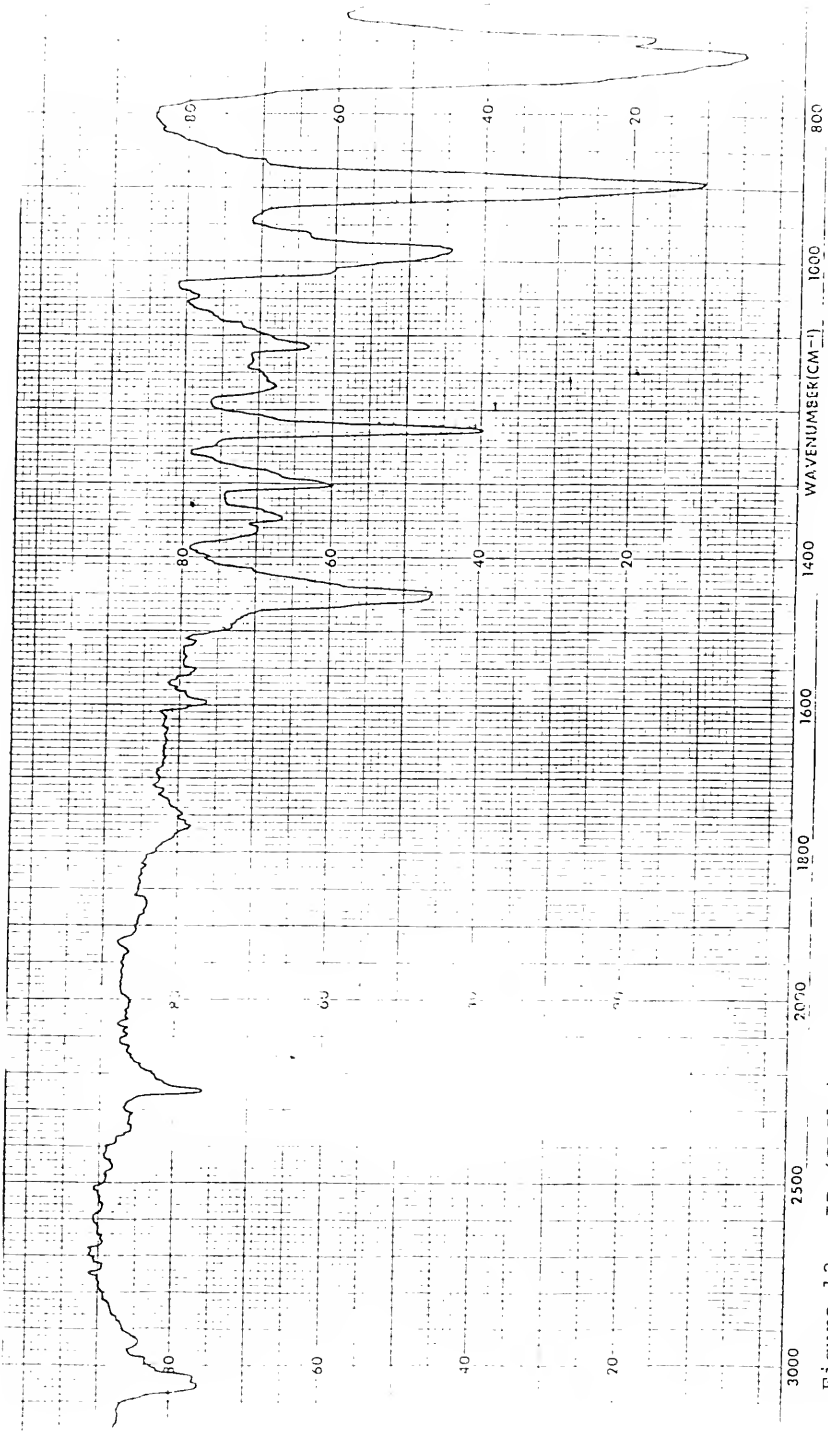


Figure 12. IR ($CDCl_3$): Endo-1,1-difluorospiro[oxabicyclo[2.2.1]]-4,7-epoxynaphthalene-6,2'cyclopropane 106.

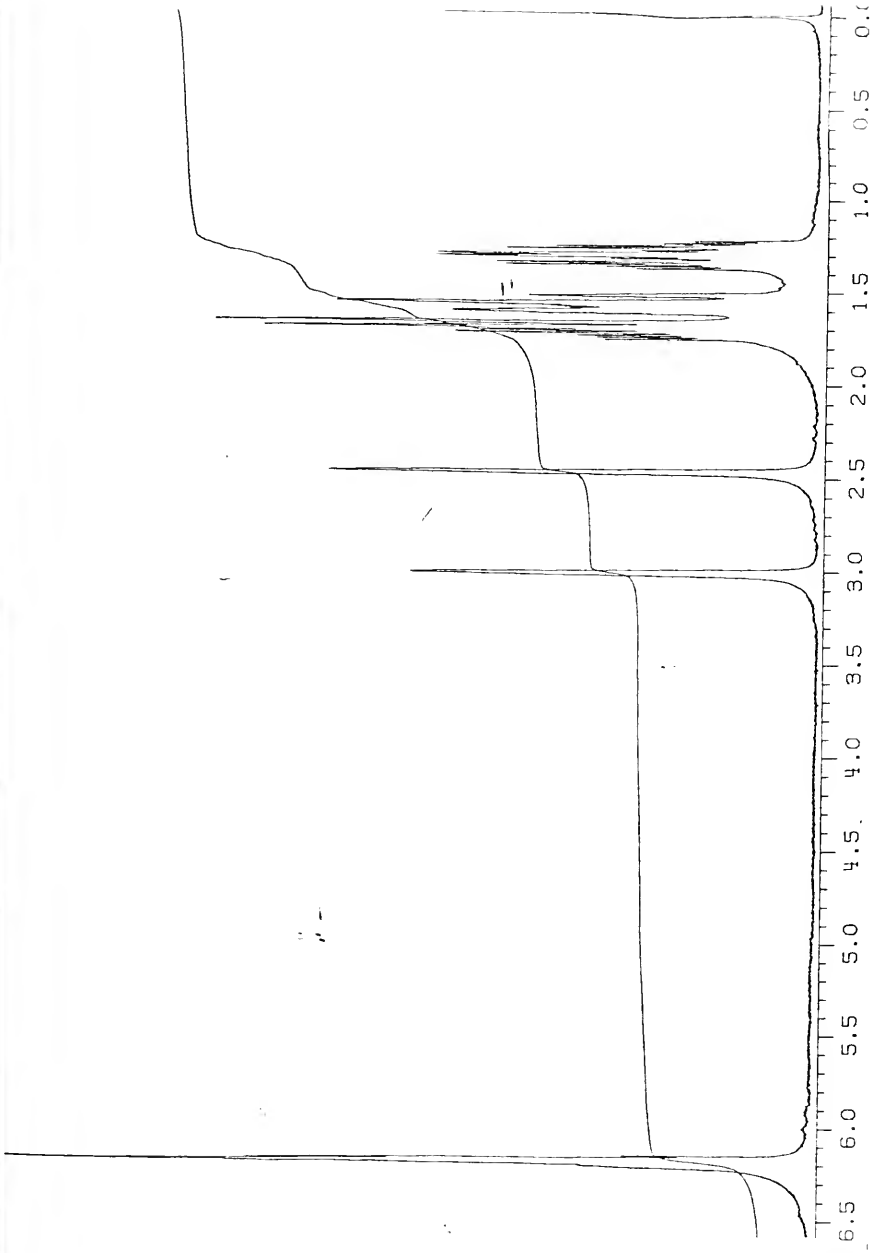


Figure 13: NMR ($CDCl_3$); 1,1-Difluorospiro[2.4]hept-2-3n3 107.

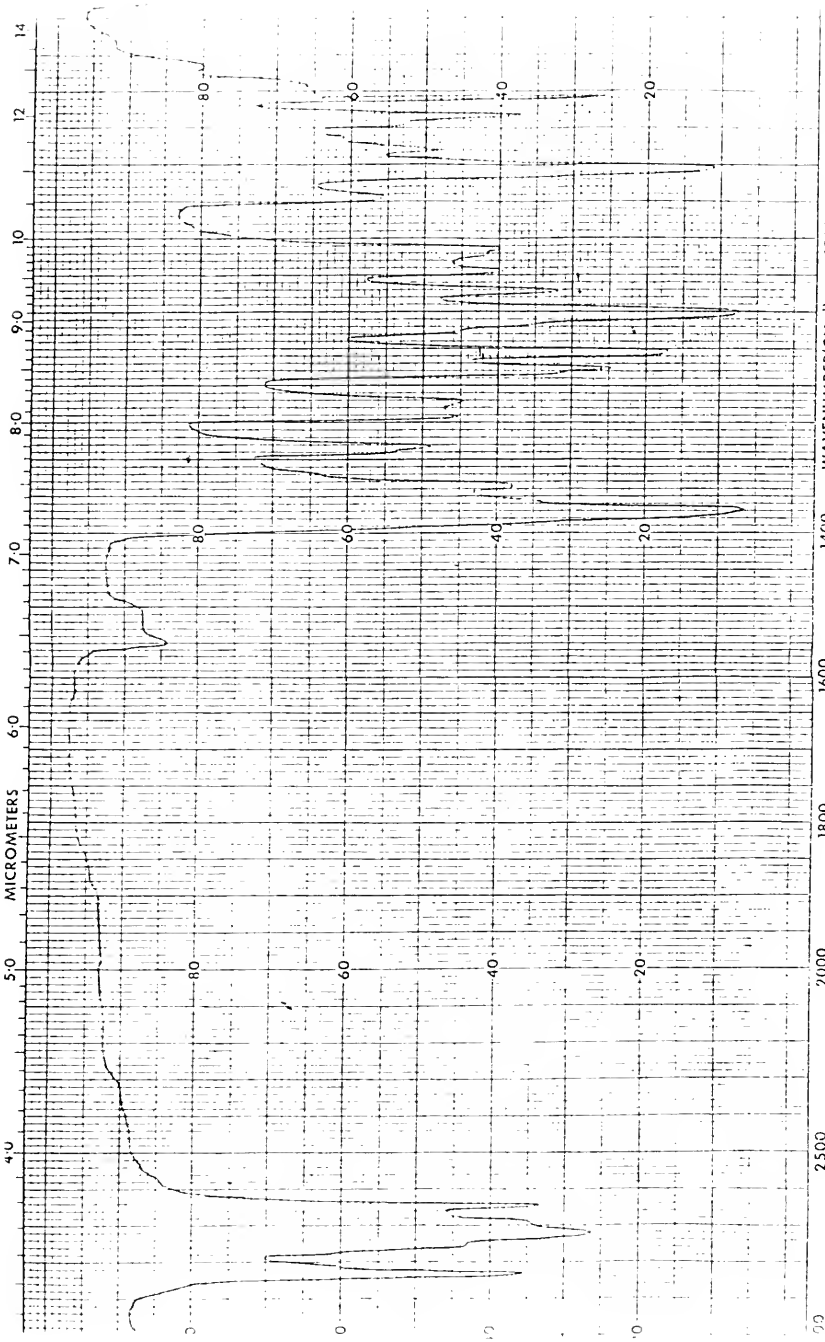


Figure 14. IR(Neat): 1,1-Difluorospiro[2.4]hept-2-ene 107.

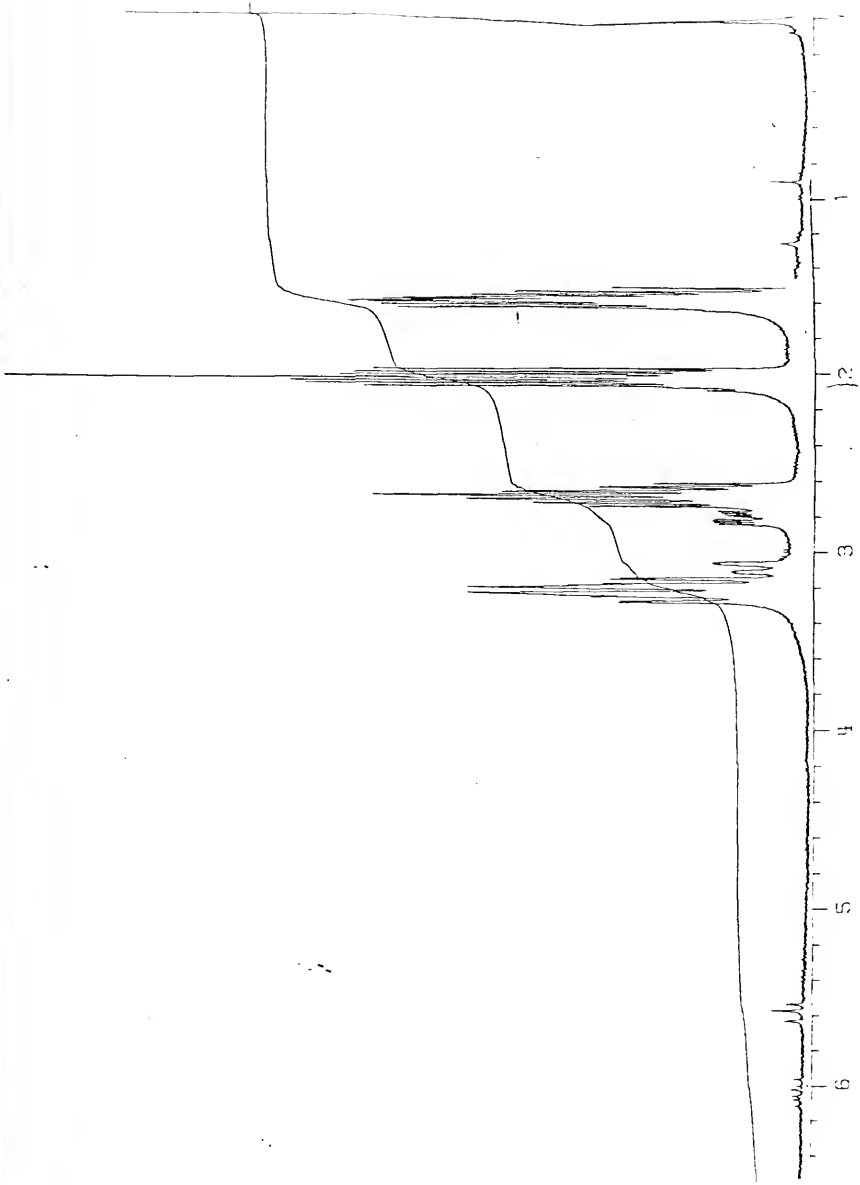


Figure 15. NMR ($CDCl_3$): 5,5-Dichloro-1,1,3,3,terafluorospiro[2.3]hexane 108.

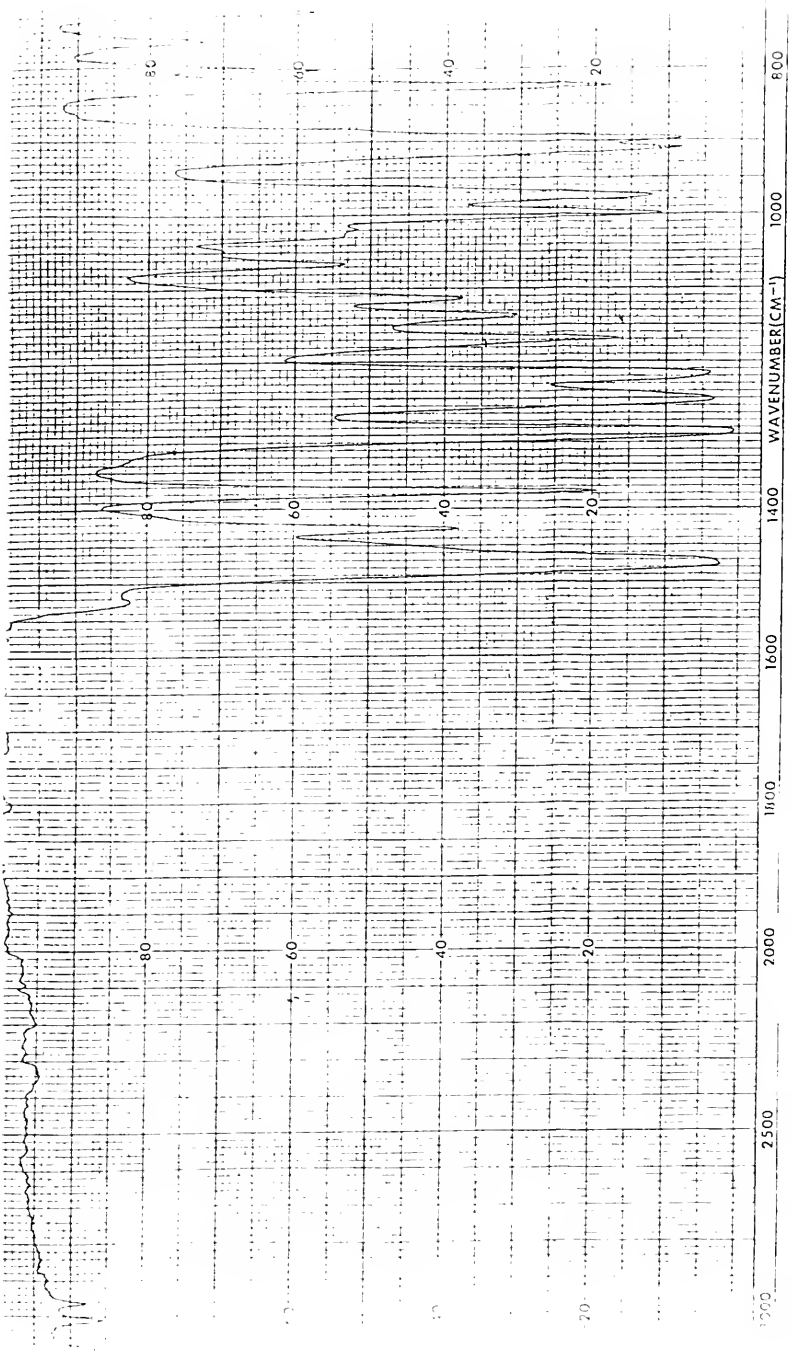


Figure 16. IR(Neat): 5,5-Dichloro-1,1,3,3,tetrafluorospiro[2.3]hexane 108.

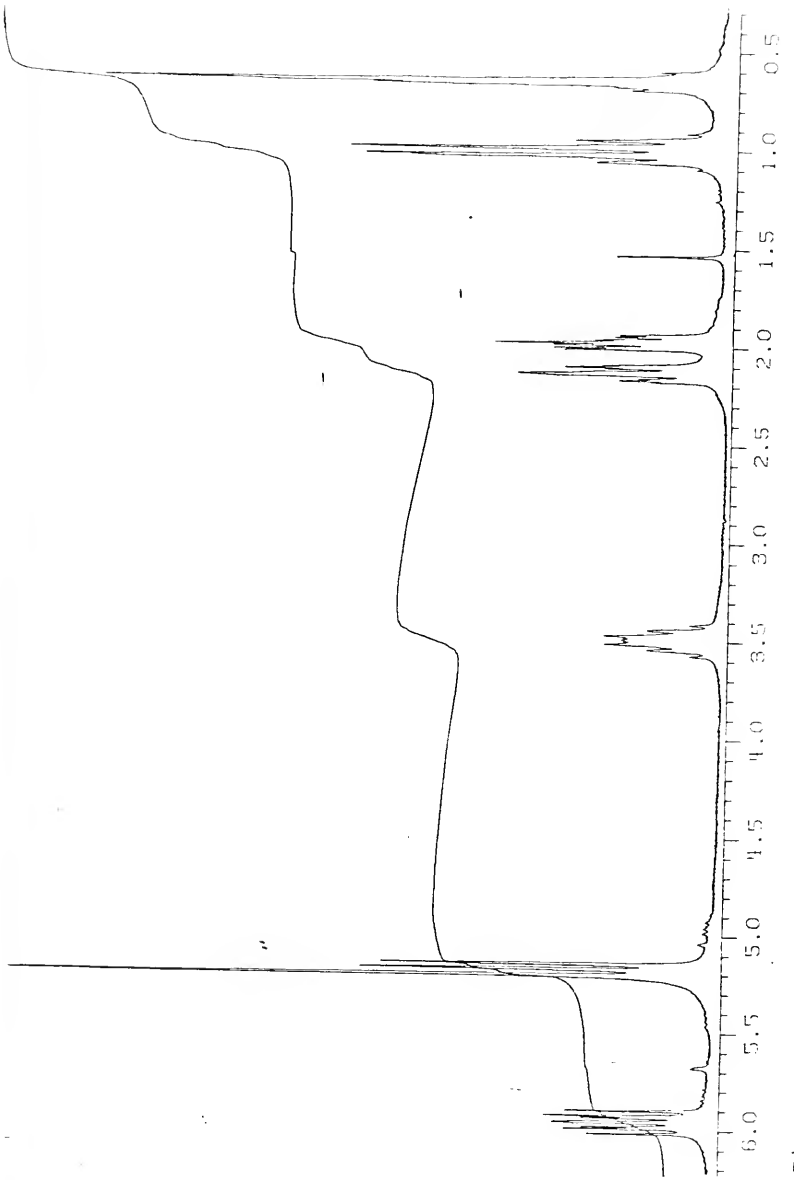


Figure 17. NMR ($CDCl_3$): 4,4-Difluoro-5-vinylspiro[2.3]hexane 109.

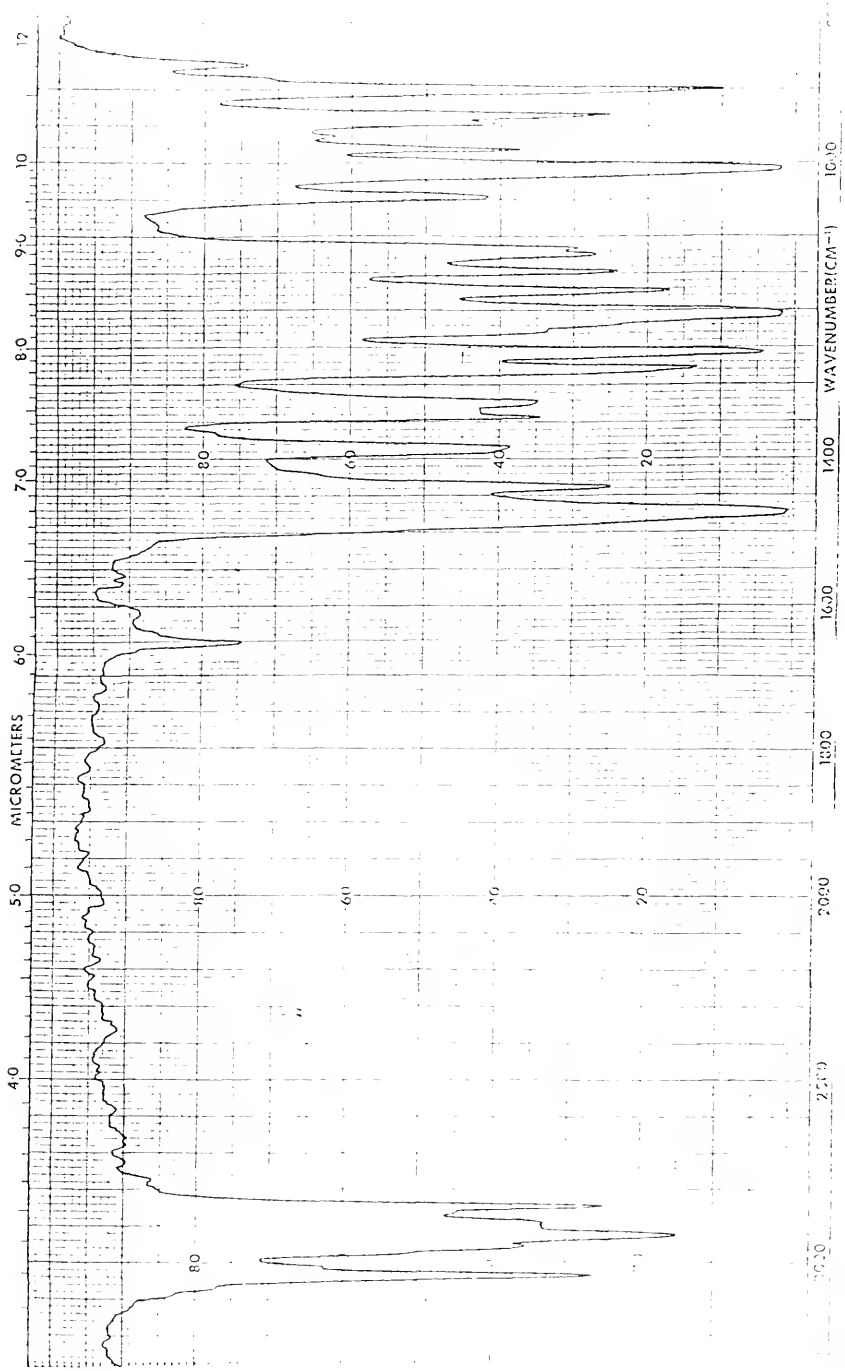


Figure 18. IR(Neat): 4,4-Difluoro-5-vinylspiro[2.2]hexane 109.

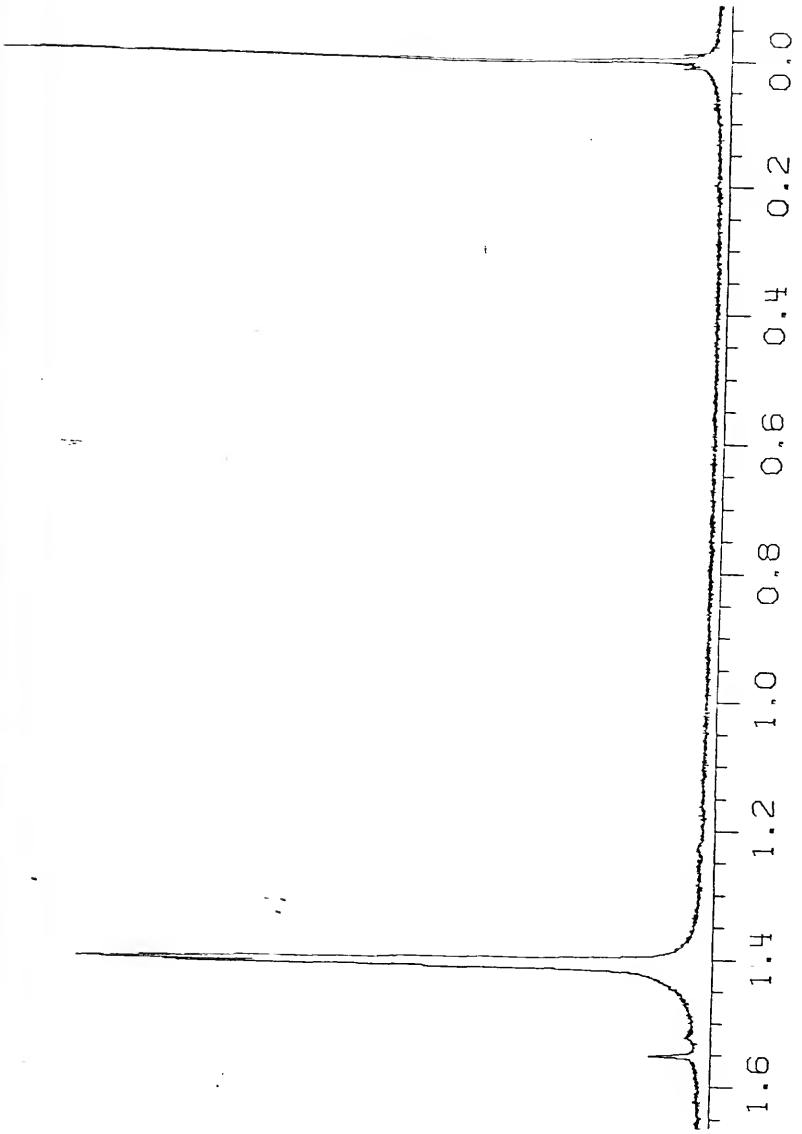


Figure 19. NMR ($CDCl_3$): 5,5-Dichloro-4,4,6,6-tetrafluorospiro[2.3]hexane 110.

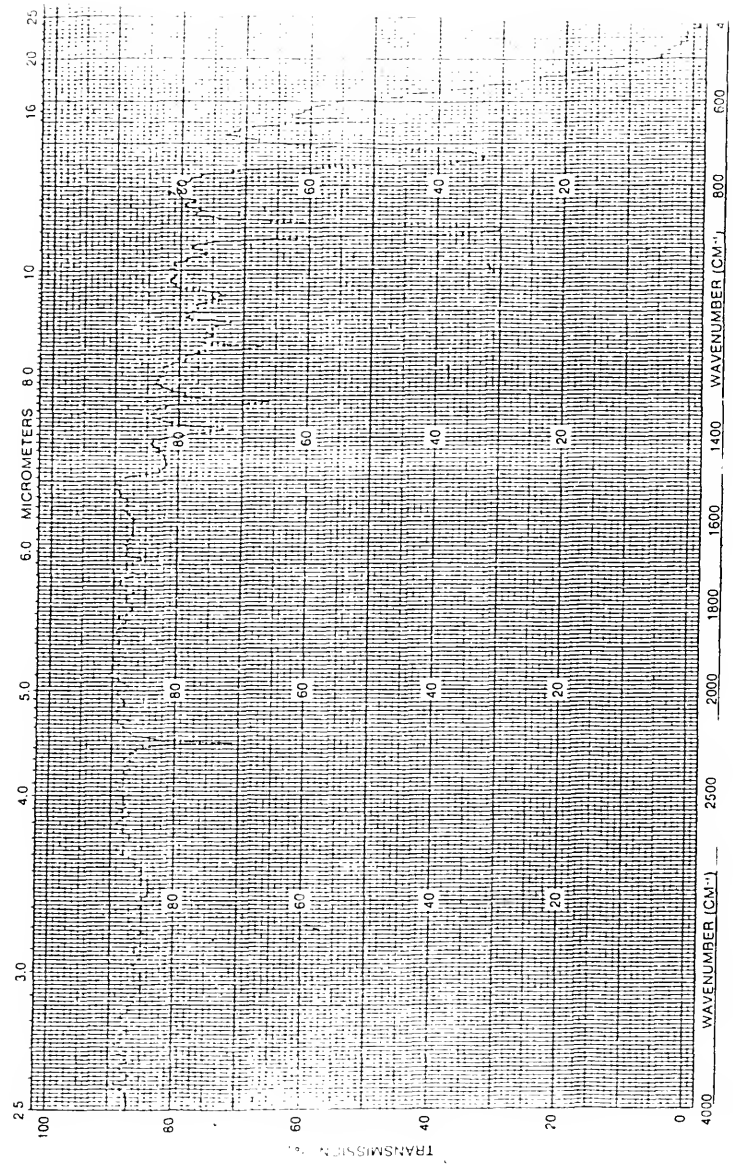


Figure 20. IR(Neat): 5,5-Dichloro-4,4,6,6-tetrafluorospiro[2.3]hexane 110.

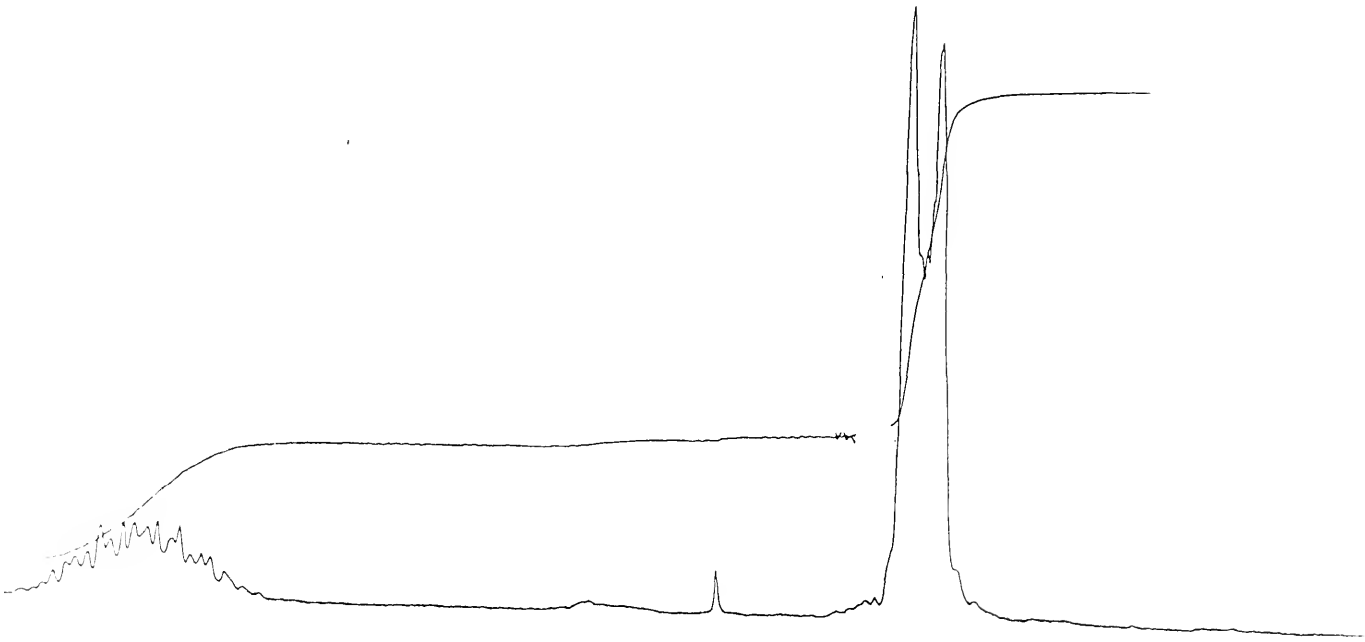


Figure 21. NMR ($CDCl_3$): cis-3,4-Dimethyl-1,1,2,2-tetrafluorocyclobutane.

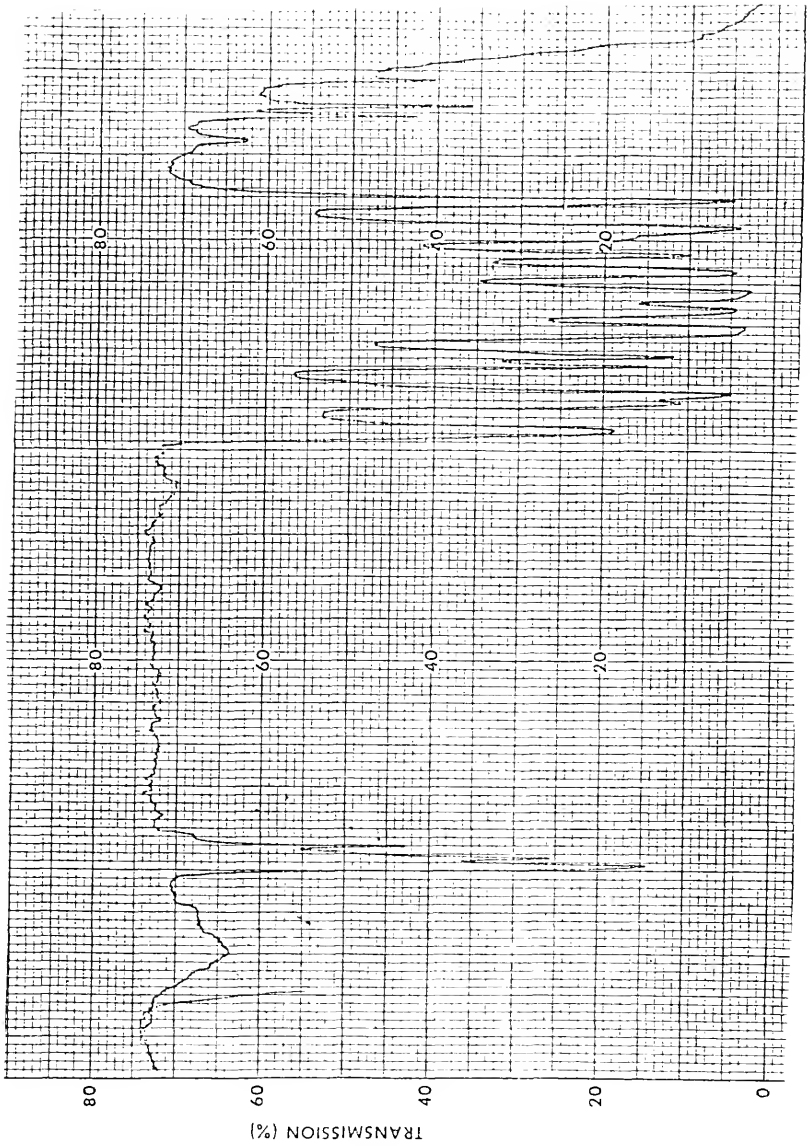


Figure 22. IR(Neat): cis-3,4-Dimethyl-1,1,2,2-tetrafluorocyclobutane.

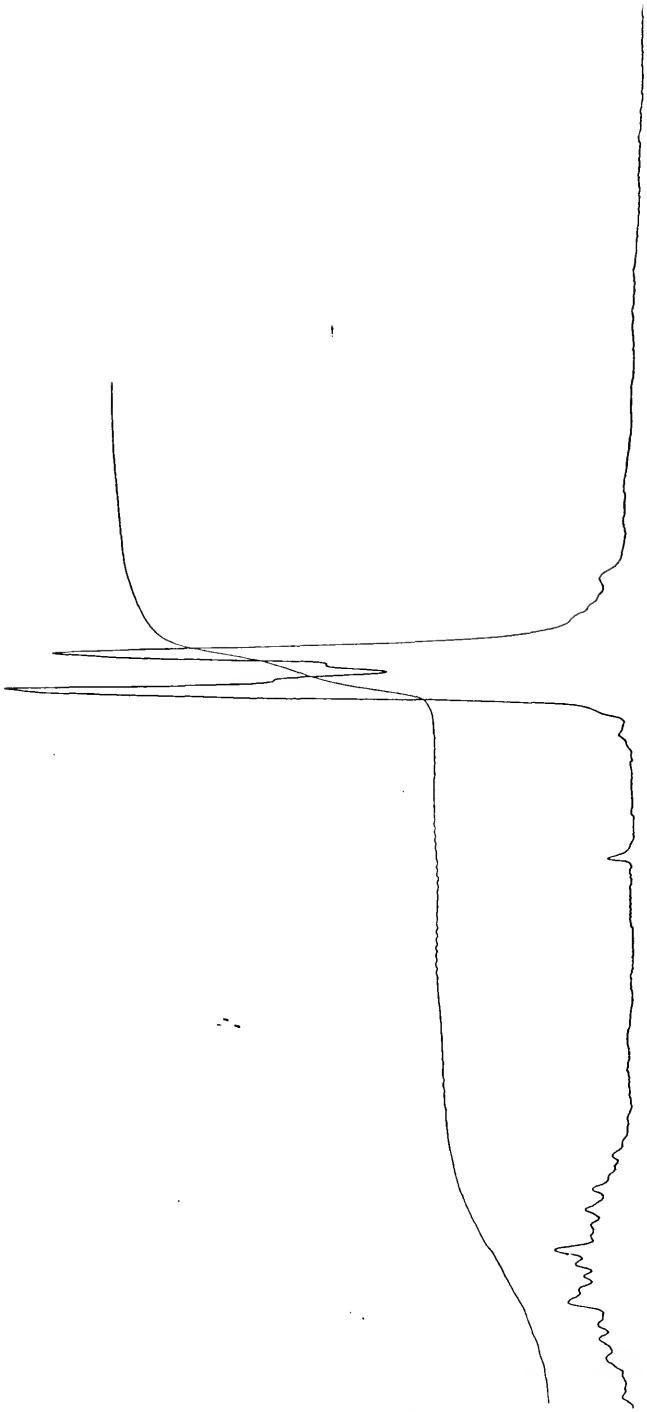


Figure 23: NMR ($CDCl_3$): trans-3,4-Dimethyl-1,1,2,2-tetrafluorocyclobutane.

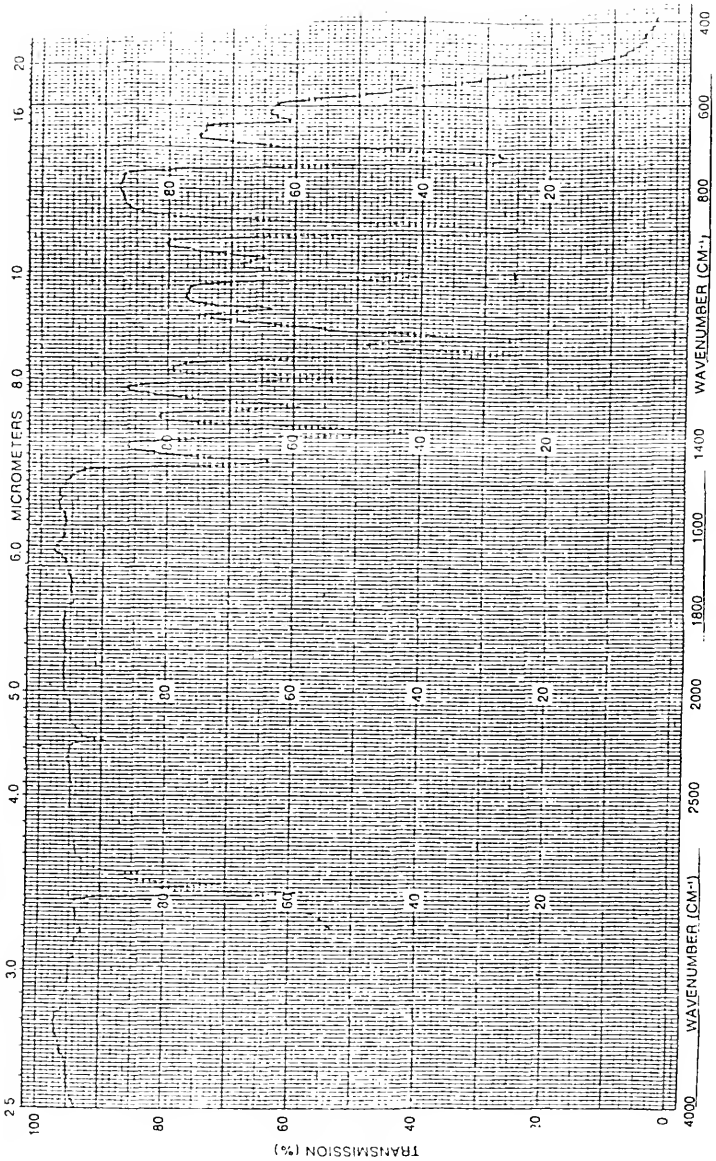


Figure 24. IR(Neat): trans-3,4-Dimethyl-1,1,2,2-tetrafluorocyclobutane.

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BIOGRAPHICAL SKETCH

Daniel Daly was born in Philadelphia, Pa., on August 3, 1952. In June of 1970, he graduated from Holy Cross High School in Riverside, New Jersey. He received the Bachelor of Science degree in chemistry and psychology from Florida State University, Tallahassee, in June of 1977. He entered graduate school in the summer of 1977 at the University of Florida. He received the Doctor of Philosophy degree in chemistry from the University of Florida in August of 1984.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William R. Dolbier, Jr.
Chairman
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

William M. Jones
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Merle A. Battiste
Professor of Chemistry

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

Charles Allen
Professor Biochemistry and Molecular Biology

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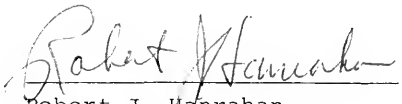

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This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School, and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

August 1984

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